Final Report

California Regional PM$_{10}$/PM$_{2.5}$ Air Quality Study – Organic Compound Measurements

Prepared for

San Joaquin Valley Air Pollution Study Agency
c/o
State of California Air Resources Board

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1. INTRODUCTION

The purpose of the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS) is to improve current scientific understanding of excessive PM levels in Central California (Watson et al., 1998). CRPAQS is an integrated effort that includes air quality and meteorological field measurements, emissions characterization, data analysis and air quality modeling. CRPAQS activities are complementary to long-term monitoring and research activities being conducted by the California Air Resources Board (ARB), the U.S. Environmental Protection Agency (EPA), the SJVUAPCD, the BAAQMD, the GBAPCD, and other air quality districts in the region. The specific objectives of the study are to:

- Provide an improved understanding of emission and dynamic atmospheric processes that influence particle formation and distribution,

- Develop and demonstrate methods useful to decision makers in formulating and comparing candidate control strategies for attaining the federal and state $PM_{10}/PM_{2.5}$ standard in central California; and

- Provide reliable means for estimating the impacts of control strategy options developed for $PM_{10}/PM_{2.5}$ on visibility, air toxics, and acidic aerosols and on attainment strategies for other regulated pollutants, notably ozone.

One of the major objectives of CRPAQS is to determine the contributions of various sources categories to episodic levels of fine particles. Reviews of available fine particle data show that carbonaceous materials account for 30% to 37% of total $PM_{2.5}$ mass in urban areas of the San Joaquin Valley (Watson, 1997). Recent studies have shown that spark-ignition vehicles (normal and high emitter and cold start emission), diesel vehicles, residential wood combustion, and meat cooking are the main sources of directly emitted carbonaceous particles (Schauer et al., 1996; Watson et al., 1998).

The receptor modeling approach requires accurate and precise measurements of the chemical composition of PM_{10} or $PM_{2.5}$ emissions from sources that are likely to contribute to high ambient PM concentrations. These source types have been identified in urban areas as: 1) motor vehicle exhaust; 2) restaurant grills and residential cooking; 3) paved road dust and entrained geological material; 4) vegetative detritus; 5) tire wear debris; and 6) wood smoke. Inorganic constituents including trace elements, sulfate, nitrate, and ammonium, and total particulate organic carbon (OC) and elemental carbon (EC) are typically measured in PM_{10} source apportionment studies. However, source contributions of carbonaceous particles, which account for the majority of fine particulate mass, are difficult to distinguish on the basis of these kinds of constituents. For example, soluble potassium, which is widely used as a wood-smoke tracer, is also present in meat cooking (Zielinska et al., 1998). Elemental and organic carbon are present in motor vehicle exhaust, wood-smoke, and other combustion-related emissions in varying proportions within the same source type. Lead and bromine additives to gasoline have served as useful tracers for motor vehicle emissions but, due to the phase-out of leaded gasoline in many parts of the U.S. in 1990, they have become

obsolete as motor vehicle emission tracers. Lowenthal et al. (1992) demonstrated the difficulty in distinguishing contributions of gasoline- and diesel-powered vehicles in complex airsheds using traditionally measured species.

For this project, the Desert Research Institute (DRI) provided equipment, sampling media and the technical support necessary for sampling and analysis of particulate and semi-volatile organic compounds (SVOC) and heavy hydrocarbons (from C_8 through C_{20}), as specified in the California Air Resources Board/San Joaquin Valleywide Air Pollution Study Agency Request for Proposals entitled, "California Regional PM_{10}/$PM_{2.5}$ Air Quality Study – Organic Compound Measurements." This project was conducted over a period of three years with field studies commencing in 12/1/99 and ending on 2/3/01. Measurements included three program elements: 1) a single composite analysis of stable particulate organic species for 24-hour samples collected every sixth day during 2000 from each of 20 satellite sampling sites; 2) four samples per day at four sites on 15 forecasted days during winter 2000-2001 for C_8-C_{20} hydrocarbons collected on Tenax cartridges and analysis by GC-FID, and fine particulate and semi-volatile organic compounds by collection on TIGF with backup PUF/XAD cartridges and analyzed by GC-MS, and 3) 24-hour samples, every sixth day from the Fresno Site during 7/1/00 to 8/31/00 for fine particulate and semi-volatile organic compounds.

1.1 Project Objectives

The overall objective of this work was to provide data on the ambient concentrations of organic compounds in the CRPAQS study domain. This data, combined with other CRPAQS measurements, will be used to refine existing conceptual models of the nature and causes of elevated particulate matter (PM) concentrations in Central California. These models address ambient gaseous and particulate organic material sources and concentrations in urban and non-urban areas, atmospheric transformations and their end-products during winter, and mixing between the surface and aloft of fresh and aged emissions. In addition, the organic compound concentration data will be used to apportion fine ($PM_{2.5}$) particulate and gaseous organic carbon, and $PM_{2.5}$ mass to emissions sources. They also provide initial and boundary conditions to exercise simulations of emissions, transport, and chemical transformations, and evaluate the accuracy of these simulations through comparison of their results with field observations.

The specific objectives of this part of CRPAQS study were to:

- Provide annual average concentrations of organic particulate compounds at the 20 satellite sampling sites;

- Provide summertime concentrations of semi-volatile organic compounds (SVOC), collected over 24-hr period on the sixth day sampling schedule at the Fresno anchor site;

- Provide SVOC, heavy hydrocarbons (from C_8 through C_{20}) concentrations collected during 15 episodic sampling days at the four anchor sites, according to the specified schedule.

2. EXPERIMENTAL

The field program phase of CRPAQS consisted of 14 months of monitoring throughout the San Joaquin Valley (SJV) and surrounding regions, as well as intensive monitoring during fall and winter-like conditions when PM_{10} and $PM_{2.5}$ concentrations are highest, and special summer organic measurements in Fresno. These field studies took place during late 1999 through early 2001. Air quality sampling locations in the annual network (December 1, 1999 through February, 2001) consisted of a combination of full scale "anchor" monitoring sites measuring both gaseous and aerosol species, plus supplemental monitoring sites measuring aerosol species using portable monitors at "satellite" sites, and monitors in a "backbone" network of ARB and air pollution control district sites. The annual program overlapped the episodic field programs. The winter episodic field study took place over a period of eight weeks on a forecast basis from mid-November 2000 through February of 2001.

2.1 Sampling Program Components and Schedules

Samples were collected during (1) a one year period during the annual field monitoring program; (2) every sixth day during the summer of 2000; and (3) several times per day during 15 episode days during the winter of 2000/2001. Measurements for the winter of 2000/2001 are discussed below.

Wintertime Episodic Sampling

Episodic sampling took place for fifteen days as selected by the CRPAQS Project Manager between 12/15/2000 and 2/6/2001 on the basis of meteorological forecasts. The contractor was given 24 to 48 hours advance notice of selected sampling days. These winter measurements were conducted at four "anchor" sites in California's Central Valley - Angiola, Fresno, Bethel Island, and Auberry (a site in the Sierra Nevada Foothills northeast of Fresno) (Watson et al., 1998). Four sequential samples were collected on each selected day with sampling periods of 0000-0500, 0500-1000, 1000-1600, and 1600-2400 PST. Samples were collected on 12/15/00-12/18/00, 12/26/00-12/28/00, 1/4/01-1/7/01 and 1/31/01-2/3/01.

The four sampling periods were selected to bracket diurnal patterns in emissions and meteorology (Watson et al., 1998). Winter flow patterns are characterized by stagnation periods interrupted by frontal passages. Most of the highest PM concentrations are found during stagnation of four to eight days duration. These stagnation periods are accompanied by strong inversions, low visibility, and high relative humidity. During winter nights and morning hours, a shallow (30 to 50 m agl) radiation inversion forms, which only begins to couple to the valley wide mixed layer between 1000 and 1200 PST, and re-asserts itself after sunset at 1800 PST (Watson et al., 1998). Pollutants are transported aloft in the afternoon, and they can spread substantially through the San Joaquin Valley in flows aloft during night and early morning. Thus, the sampling periods from 0500 to 1000 PST and 1000 to 1600 PST attempt to capture fresh emissions (especially important at the urban sites), and the

emissions dispersion, respectively. The sampling periods from 1600 to 2400 and 0000 to 0500 PST correspond to the formation and tightening of the radiation inversion layer, respectively.

These flows aloft and afternoon mixing are consistent with diurnal variations in particle chemistry (Watson et al., 1998). Primary emissions (as assessed from elemental carbon concentrations) are often highest during nighttime and morning hours in the cities, and lowest in the non-urban sites. Several afternoon samples showed a decrease in elemental carbon in urban sites, but a slight increase in non-urban sites. This observation is consistent with the major sources of elemental carbon being urban emissions that accumulate in the shallow surface layer at the early morning then mix aloft in the afternoon. Once aloft, these emissions are effectively separated from the surface by a re-formation of a surface layer after sunset. They can also be transported throughout the valley and mix to the surface at non-urban sites during afternoon mixing of subsequent days (Watson et al., 1998).

Fresno is an urban site, located in a residential/commercial area (Watson et al., 1998), and is influenced by a broad mixture of neighborhood, urban and regional scale $PM_{2.5}$ sources. The Angiola site is located in a non-urban setting, with a variety of surrounding agricultural activities. The Bethel Inland site, characterized as an interbasin transport site, is located in the Sacramento Delta area, in the transition area between the Bay Area and the San Joaquin Valley. It is isolated from local sources, but is directly east of the Benicia/Martinez, Pittsburg, Antioch industrial corridor where most of the Central California point source emissions are located. Auberry, the Sierra Foothills background site, is northeast of Fresno, at 637 m (2090 feet) above mean sea level. This site can be either above or below inversion layer, depending on the meteorological conditions. There is a potential for observing a noticeable difference between pollutants and concentrations, depending on this site being above or below inversion layer.

2.2 $PM_{2.5}$ Semi-Volatile Organic Compounds (W) Sampling

$PM_{2.5}$ Semi-Volatile Organic Compounds (designated as "W" by Watson et al., 1998) were collected during 15 episode days at the four anchor sites. The term "Semi-Volatile Organic Compounds" (SVOC) refers to those compounds that are distributed between the gas and particle phases. Two to four ring PAH, methoxy-phenol derivatives, and some organic acids are distributed between the vapor and particulate phases, whereas hopanes, steranes, cholesterol high MW organic acids, and high MW alkanes are present exclusively in the particulate phase. Thus, the use of a filter followed by a back-up solid adsorbent is necessary to account for the total ambient concentrations of these species.

Filter media for collecting particle-associated PAH must have high collection efficiency for particles in the respirable size range and exhibit minimal differential pressure drop over a sampling period. In addition, the filter substrate must be inert to minimize artifact formation during sampling. Teflon-impregnated glass-fiber filters (Offermann et al., 1990) and quartz filters (Wilson et al., 1990) have been recommended for PAH collection. TIGF filters are easier to use and they were employed successfully in many ambient PAH monitoring programs (see, for example, Atkinson et al., 1988; Arey et al., 1987, 1988, 1989;

Zielinska et al., 1989). Pall Gelman (Ann Arbor, MI) T60A20 100 mm diameter Teflon-impregnated glass fiber (TIGF) filters were used.

A variety of back-up solid adsorbents have been used to collect gaseous PAH and those PAH which are volatilized off the filter during sampling. Polyurethane foam (PUF), widely used for sampling semi-volatile PAH in outdoor air, is easy to handle in the field, has low resistance to the air flow, is inexpensive, and is easy to clean and store, but its collection efficiency for the more volatile PAH is low (Chuang et al., 1987; Atkinson et al., 1988). Polystyrene-divinylbenzene resins, XAD-2 and XAD-4, have been reported to have a high collection efficiency for PAH (Offermann et al., 1990; Chuang et al., 1987, 1990). A collection of SVOC using polyurethane foam–granular adsorbent sandwich cartridges (Zaranski et al., 1991) has been also reported. Good collection efficiencies for naphthalene using either Tenax-GC or XAD resins have been reported. Since we have successfully used PUF/XAD-4/PUF cartridges for collection of semi-volatile PAH (including naphthalene) in our ambient monitoring program in Arizona since the spring of 1994, and during NFRAQS in winter 1997, we used this same resin in combination with PUF in this study. The PUF sheets were purchased from E.R. Carpenter Company, Inc. (Richmond, VA) and cut into 2" diameter plugs at DRI. The Amberlite XAD-4 resin (20-60 mesh) was purchased from Aldrich Chemical Company, Inc. PUF plugs and XAD resins were cleaned before sampling, as described below.

Teflon-impregnated glass fiber (TIGF) filters were cleaned by sonication for 10 minutes in dichloromethane (CH_2Cl_2) twice, with the solvent drained and replaced, and sonicated for 10 minutes in methanol twice with the solvent drained and replaced. Filters were then dried in a vacuum oven at −15 to −20 in Hg for minimum of 24 hours, and then placed in Uline metallic ZipTop static shielding bags, stored in aluminum cans in freezer.

PUF plugs were cleaned by first washing with distilled water, followed by Soxhlet extraction for 48 hours with acetone and followed by Soxhlet extraction for 48 hours with 10% diethyl ether in hexane under the same conditions. The extracted PUF plugs were dried in a vacuum oven at -15 to −20 in Hg, 50° C for approximately 3 days or until no solvent odor was detected. If storage was necessary, PUF plugs were stored in clean 1L glass jars with Teflon lined lids wrapped in aluminum foil. Powder-free nitrile gloves were worn at all times when handling PUF plugs.

XAD-4 was placed in a Buchner funnel and rinsed with distilled water three times followed by technical grade methanol 3-4 times, and again three times with distilled water. It was then put into clean nylon stockings and further cleaned by Soxhlet extraction for 48 hours with methanol. It was then Soxhlet extracted for another 48 hours using dichloromethane (CH_2Cl_2) followed by Soxhlet extraction in acetone for 48 hours. The XAD-4 was then dried in a vacuum oven at −15 to −20 in Hg and 50 °C. Cleaned XAD-4 was transferred to clean 1L glass jars and stored in aluminum cans with activated charcoal.

An aliquot of each batch of cleaned XAD-4, PUF, and TIGF filters was then extracted and checked by GC/MS for purity. Any batch determined to have excessive impurities (more than 10 μg of naphthalene) was re-cleaned and re-checked for purity.

The DRI Sequential fine particle/semi-volatile organic sampler was used in this study to collect semi-volatile organic compounds. This is a multiple-event sampler, with the pump downstream of the PUF/XAD/PUF cartridge, allowing unattended collection of up to four samples. Flow can be individually adjusted for each sample. The flow rates were measured before and after each run using a calibrated mass flow meter and the mean value was used to calculate volumes of air sampled.

2.2.1 Heavy Hydrocarbons (V) Sampling

Heavy hydrocarbons, defined as hydrocarbons in the range of C_8 to C_{20} (designated as "V" by Watson et al., 1998), were collected during 15 episode days at the four anchor sites. These species were collected using Tenax-TA (Alltech) solid adsorbent that is characterized by better adsorption properties than Tenax-GC. Tenax-TA is designed primarily as a trapping agent, whereas Tenax-GC, the original Tenax, was designed both for GC column packing and for adsorbent traps.

For Tenax-TA cartridges, the safe sampling volume (i.e., the volume of air that may be sampled over a variety of circumstances without significant breakthrough of compounds of interest) can be roughly estimated from data published in the literature (Brown and Purnell, 1979; Krost et al., 1982; U.S. EPA Method TO-1). The most volatile compounds of interest for solid adsorbent collection are, for this study, C_8-C_9 aromatic and aliphatic hydrocarbons, such as ethylbenzene (C8, b.p. 136.2 °C), cumene (isopropylbenzene, C_9, b.p. 152 °C), and isomeric C_9 alkanes and alkenes (b.p. in the range of 140-150 °C). The breakthrough volume for ethylbenzene at 50 °F (10 °C) and 70 °F (21.1 °C) is 1393 L and 693 L, respectively, of air per gram of Tenax (Krost et al., 1982). Using a 1.5 safety factor recommended by U.S. EPA Method TO-1, the safe sampling volume for ethylbenzene at 50 °F and 70 °F was calculated to be 185.7 L and 92.4 L, respectively, of air for 0.2 g of Tenax used. The range of temperature from 50 °F to 70 °F is expected to be the most likely to occur during wintertime in the SJV area. That means that a flow rate of ~0.25 L/min could be employed over a sampling time of six hours.

For this study, two Tenax cartridges connected in series were used for approximately 10% of all samples collected at the Sierra Nevada Foothills site, since this method allowed semi-quantitative evaluation of inadequate retention of a given compound.

Prior to use, the Tenax-TA solid adsorbent was cleaned by Soxhlet extraction with hexane/acetone mixture (4/1 v/v) overnight, and dried in a vacuum oven at ~80 °C. The dry Tenax was packed into Pyrex glass tubes (4 mm i.d. x 15 cm long, each tube containing 0.2 g of Tenax) and thermally conditioned for a minimum of four hours by heating in an oven at 300 °C under nitrogen purge (25 ml/min nitrogen flow). Approximately 10% of the precleaned Tenax cartridges were tested by GC/FID for purity prior to sampling. After cleaning, the Tenax cartridges were capped tightly using clean Swagelok caps (brass) with

graphite/vespel ferrules, placed in metal containers with activated charcoal on the bottom, and kept in a clean environment at room temperature until use.

The DRI Sequential Tenax sampler was used in this study to collect heavy hydrocarbon samples. This is a multiple-event sampler, with the pump downstream of the Tenax, allowing unattended collection of up to six samples. The six-port manifold and flow control device allows six cartridges to be attached at once. Flow can be individually adjusted for each cartridge. The flow rates were measured before and after each run using a calibrated mass flow meter and the mean value was used to calculate volumes of air sampled. Tenax cartridges installed in the sampler were protected by a check valve upstream, and a solenoid valve downstream. They were only exposed to the air stream during the period of sampling. Each solenoid was controlled separately by the timer and can sample independently.

When the exposed cartridges were removed, they were immediately plugged with Swagelok caps, and stored in a can designated for exposed cartridges with activated charcoal on the bottom. The exposed cartridges were stored inside a refrigerator and returned to the laboratory in a cooler.

2.2.2 Sample Analysis

2.2.2.1   Analysis of PM$_{2.5}$ and Semi-Volatile Organic Compounds

For each sample, PUF/XAD/PUF cartridge and TIGF filter was extracted and analyzed together. The method of particulate matter sampling that uses a filter followed by a solid adsorbent trap does not provide the true gas- and particle phase distribution of SVOC. The particles collected on a filter are subjected to two types of artifacts: (1) a positive artifact, due to the adsorption of gaseous compounds on deposited particles or on the filter material itself; and (2) a negative artifact, due to the volatilization (or blow-off) the particle phase species during collection during the sampling process. Thus, the analysis of the PUF/XAD/PUF cartridges and filters separately would produce biased results as far as gas-particle phase distribution of individual species is concerned. The main reason for using the solid adsorbent following the filter for SVOC collection was to account for a total atmospheric concentration of SVOC.

Prior to extraction, the following deuterated internal standards were added to each filter-sorbent pair: naphthalene-d$_8$, acenaphthylene-d$_8$, phenanthrene-d$_{10}$, anthracene-d$_{10}$, chrysene-d$_{12}$, fluoranthene-d$_{10}$, pyrene-d$_{10}$, benz[a]anthracene-d$_{12}$, benzo[e]pyrene-d$_{12}$, benzo[a]pyrene-d$_{12}$, benzo[k]fluoranthene-d$_{12}$, coronene-d$_{12}$, benzo[g,h,i]perylene-d$_{12}$, n-tetracosane- d$_{50}$, n-hexanoic acid- d$_{11}$, n-decanoic acid- d$_{19}$, benzoic acid - d$_5$ $_a$, and levoglucosan U-C$_{13}$. Since PUF should not be extracted with dichloromethane, as they tend to disintegrate in this solvent, the PUF plugs were Soxhlet extracted separately with 10% diethyl ether in hexane, followed by acetone and the filter-XAD pairs were microwave extracted with dichloromethane, followed by acetone.

The solvent extracts from the PUF plugs and filter—XAD pairs for individual samples were combined, concentrated by rotary evaporation at 20 °C under gentle vacuum to ~1 mL and filtered through a 0.2 μm PTFE disposable filter device (Whatman Pura disc^{TM}

25TF), rinsing the flask 3 times with 1 ml dichloromethane and acetone (50/50 by volume) each time. Filtrate is collected in a 4 mL amber glass vial for a total volume of ~4 mL. Approximately 200 µL of acetonitrile was added to the sample and placed under a gentle stream of nitrogen to reduce the volume to 1 mL. The samples were then split into two equivalent fractions. The final sample volume of both halves was adjusted to 0.1 mL with acetonitrile.

The non-derivatized SVOC fraction was analyzed by EI (electron impact) GC/MS technique for PAH, hopanes, sterames, and high MW alkanes. A Varian CP 3800 GC equipped with an 8200CX Automatic Sampler and interfaced to a Varian Saturn 2000 Ion Trap was used for these analyses. Injections (1 µL) were made in the splitless mode onto a 5% phenylmethylsilicone fused-silica capillary column (CP-Sil 8 Chrompack (30m x 0.25mm x 0.25 mm), Varian Inc.). Quantification of the PAH, hopanes, steranes, and high MW alkanes was obtained by selective ion storage (SIS) technique, monitoring the molecular ion of each compound of interest and corresponding deuterated internal standard, added prior to extraction.

The fraction for the polar analysis was derivatized using a mixture of bis(trimethylsilyl) trifluoroacetamide and pyridine to convert the polar compounds into their trimethylsilyl derivatives for analysis of organic acids, cholesterol, sitosterol, and levoglucosan. The extract was reduced to a volume of 50 µL under a gentle stream of ultra-high purity (UHP) nitrogen with a water trap (Chrompack CP-Gas-Clean moisture filter 17971.   50 µL of silylation grade pyridine and 150 µL of bis(trimethylsilyl) trifluoroacetamide was added to each sample vial and immediately capped. The sample was then placed into thermal plates (custom made) containing individual vial wells with the temperature maintained at 70°C for 3 hours. The samples were then analyzed by GC/MS within18 hours.

The derivatized SVOC fraction was analyzed by CI (chemical ionization) GC/MS technique with isobutane for polar organics including organic acids, cholesterol, sitosterol, and levoglucosan. The CI technique provides improved minimum detection limits for oxygenated compounds. A Varian CP 3800 GC equipped with an 8400 Automatic Sampler and interfaced to a Varian Saturn 2000 Ion Trap was used for these analyses. Injections (1 µL) were made in the splitless mode onto a 5% phenylmethylsilicone fused-silica capillary column (CP-Sil 8 Chrompack (30m x 0.25mm x 0.25 mm), Varian Inc.). Quantification of the organic acids, cholesterol, sitosterol, and levoglucosan was obtained by a selective ion storage (SIS) technique, monitoring the molecular ion of each compound of interest and corresponding deuterated internal standard, added prior to extraction.

The choice of the derivatization reagent BSTFA for polar organics was made due to its reactivity with the hydroxyl functional group. The reaction involves a replacement of the hydroxyl hydrogen with a trimethylsilyl group. This replacement transforms organic acids, levoglucosan, and cholesterol into more non-polar and more volatile derivatives, thus enhancing the chromatography. Identification was then further enhanced by mass spectral isobutane chemical ionization, providing a soft fragmentation. A strong presence of the molecular ion (M+) was found in most spectra. In addition, the spectra of most organic acids contained a high abundance of (M-15)+ fragment ion, corresponding to a loss of methyl

group. Even though the compounds reported here were all quantified using authentic standards, the soft fragmentation of these analytes provided additional evidence for positive identification. Table 2-1 provides a list of the polar organic compounds and the quantification ions used for identification.

Table 2-1. List of Polar Organics.

Compound Type	Mnemonic	Compound Name	Quantitation Ion
IS		hexanoic-d11 acid	200
Analyte	HEXAC	hexanoic acid	173, 189
Analyte	HEPTAC	heptanoic acid	203, 187
Analyte	MEMALON	methylmalonic acid	263
Analyte	GUAI	Guaiacol	181, 196
IS		benzoic-d5 acid	184, 200
Analyte	BENAC	benzoic acid	179, 195
Analyte	OCTANAC	octanoic acid	201, 289
Analyte	GLYCERO	Glycerol	309, 293
Analyte	MALEAC	maleic acid	261
IS		succinic-d4 acid	251, 267
Analyte	SUCAC	succinic acid	173, 263
Analyte	MEGUA4	4-methylguaiacol	210, 195
Analyte	MESUCAC	methylsuccinic acid	187, 349
Analyte	OTOLUIC	o-toluic acid	281
Analyte	PICAC	picolinic acid	196
Analyte	MTOLUIC	m-toluic acid	281
Recovery Std.		1,2,4-butanetriol	233, 307
Analyte	NONAC	nonanoic acid	231, 215
Analyte	PTOLUIC	p-toluic acid	281
Analyte	MEPIC36	3-, 6-methylpicolinic acid	250
Analyte	DIMEB26	2,6-dimethylbenzoic acid	295
Analyte	ETGUA4	4-ethyl-guaiacol	224, 209
Analyte	SYRI	Syringol	211, 226
Analyte	GLUAC	glutaric acid	187, 261
Analyte	MEGLU2	2-methylglutaric acid	331, 275
Analyte	DIMEB25	2,5-dimethylbenzoic acid	295
Analyte	MEGLU3	3-methylglutaric acid	275, 331
Analyte	DIMEB24	2,4-dimethylbenzoic acid	295
Analyte	DIMEB35	3,5-dimethylbenzoic acid	295
Analyte	DIMEB23	2,3-dimethylbenzoic acid	295
Analyte	DECAC	decanoic acid	245, 229
Analyte	ALGUAI4	4-allyl-guaiacol (eugenol)	221, 236
Analyte	MESYR4	4-methyl-syringol	241, 224
Analyte	DIMEB34	3,4-dimethylbenzoic acid	295
Analyte	HEXDAC	hexanedioic (adipic) acid	201, 291
Analyte	TDECEN2	trans-2-decenoic acid	243, 227
Analyte	CPINAC	cis-pinonic acid	257, 239
Analyte	MEADIP3	3-methyladipic acid	289, 305
Analyte	FGUAI4	4-formyl-guaiacol (vanillin)	225
Analyte	UNDEC	undecanoic acid	243, 259
Analyte	ISEUG	Isoeugenol	236, 221
Analyte	HEPDAC	Heptanedioic (pimelic) acid	215, 305
Analyte	ACVAN	acetovanillone	239, 223
Analyte	LAUAC	dodecanoic (lauric) acid	273, 257
Analyte	PHTHAC	phthalic acid	295

Compound Type	Mnemonic	Compound Name	Quantitation Ion
IS		Levoglucosan-U-13C6	295, 367
Analyte	LEVG	Levoglucosan	289, 361
Analyte	SYRALD	syringaldehyde	255, 327
Analyte	TDECAC	tridecanoic acid	287, 271
Analyte	ISPHAC	isophthalic acid	295, 311
Analyte	AZEAC	azelaic acid	243, 333
Analyte	MYROL	myristoleic acid	299
IS		myristic-d27 acid	328, 312
Analyte	MYRAC	myristic acid	301, 285
Analyte	SEBAC	sebacic acid	257, 347
Analyte	PDECAC	pentadecanoic acid	315, 299
Analyte	UNDECDI	undecanedioic acid	271
Analyte	PALOL	palmitoleic acid	327, 311
Analyte	PALAC	palmitic acid	329, 313
Analyte	ISSTER	isostearic acid	357, 341
Analyte	HEPTAD	heptadecanoic acid	341, 327
Analyte	UNDD111	1,11-undecanedicarboxylic acid	299
Analyte	OLAC	oleic acid	355
Analyte	ELAC	elaidic acid	355
Analyte	STEAC	stearic acid	357, 341
Analyte	DODD112	1,12-dodceanedicarboxylic acid	313
Analyte	NDECAC	nonadecanoic acid	371, 355
Analyte	DHABAC	dehydroabietic acid	373
Analyte	ECOSAC	eicosanoic acid	385, 370
Analyte	ABAC	abietic acid	375, 359
IS		cholesterol-d6	464, 448
Analyte	CHOL	Cholesterol	458, 444
Analyte	BSIT	b-sitosterol	397, 486

Calibration curves for GC/MS quantification were made for the molecular ion peaks of the PAH and all other compounds of interest using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as internal standards. Individual neat standards were purchased and used to make calibration solutions. A six level calibration was performed for each compound of interest and the calibration check (using a median calibration solution of standards) was run every ten samples to check for accuracy of the analyses. If the relative accuracy of measurement (defined as a percentage difference from the standard value) was less than 20%, the instrument was recalibrated and samples were reanalyzed.

2.2.2.2 Analysis of Tenax Samples for Heavy Hydrocarbons

Tenax samples were analyzed by the thermal desorption-cryogenic preconcentration method, followed by high-resolution gas chromatographic separation and flame ionization detection (FID) of individual hydrocarbons. The Chrompack Thermal Desorption-Cold Trap Injection (TCT) unit, which was attached to the GC/FID system, was used for the purpose of sample desorption and cryogenic preconcentration. A 60 m (0.32 mm i.d., 0.25 mm film thickness) DB-1 capillary column (J&W Scientific, Inc.) was used to achieve separation of the target species. For calibration of the GC/FID, a set of standard Tenax cartridges were prepared by spiking the cartridges with a methanol solution of 1,2,4-trimethylbenzene and n-dodecane, prepared from high-purity commercially available hydrocarbons (Alltech

Associates, Inc.). The calibration was based on the uniform response of FID detector to carbon atoms. The FID response factor per one nanomole of carbon was determined experimentally, using n-dodecane and 1,2,4-trimethylbenzene deposited on Tenax cartridges. Three different concentrations (plus one blank) were used to construct calibration curves. The response factor per one nanomole of carbon for each compound used for calibration was averaged to give one uniform response factor for all hydrocarbons (both aliphatic and aromatic). In addition, standard prepared Tenax cartridges spiked with 1,2,4-trimethylbenzene and n-dodecane were periodically analyzed by GC/FID to verify quantitative recovery of these hydrocarbons from the cartridges.

3.   RESULTS

Samples were collected: (1) during a one year period during the annual field monitoring program; (2) every sixth day during the summer of 2000; and (3) several times per day during 15 episode days during the winter of 2000/2001. Episodic sampling was conducted at the four anchor sites in California's Central Valley: Angiola, Fresno, Bethel Island, and Auberry (a site in the Sierra Nevada Foothills northeast of Fresno) to determine their ambient concentrations during days in which high PM levels were forecast.

3.1   Semi-Volatile Organic Analysis

Polycyclic aromatic hydrocarbons (PAH) are formed during the combustion process and as such are potential tracers for various combustion emissions. Many of these compounds are found in all combustion sources but have variable proportions. Further information can be obtained by the analysis of additional classes of compounds such as methoxylated phenol derivatives, organic acids, sterols, high MW alkanes, hopanes and levoglucosan. Many of the hydrocarbon compounds analyzed, such as normal and branched alkanes, are common to many emission sources. However, normal alkanes may provide information regarding the nature of the emission source. Biogenic emissions are reported to have an even-odd carbon number preference, but anthropogenic emissions do not show an even-odd preference (Mazurek and Simoneit, 1984). Methoxylated phenol derivatives are reported to be associated with wood combustion and may aid in differentiation between soft and hard woods (Hawthorne et al., 1988 &1989). In addition, levoglucosan has been reported to be unique to wood combustion and found to be in relatively high amounts among biomass species sampled (Simoneit et al., 1999; Fine et al., 2002). Cholesterol and organic acids, which are found in tissues of higher animals, may aid in the apportionment of meat cooking sources (Rogge et al., 1991; McDonald et al., 2003). Hopane and sterane compounds have been used for the unique identification of oils and oil shale by geochemists for many years. These compounds may provide a unique marker for mobile sources such as gasoline and diesel vehicles due to their presence in lubricating oils (Rogge et al., 1993; Schauer et al., 2002). Additional information may be gathered from the analysis of organic acids, which are emitted in high abundance relative to many of the other identifiable semi-volatile organic compounds (Nolte et al., 1999; Fraser et al., 2003). These compounds are emitted in many of the combustion emissions, however unique proportions of organic acids may exist for various emission sources.

Results from one of the five episodes collected at the Fresno site are presented in this section to illustrate the variances in certain organics with possible source contributions and meteorological conditions. As previously mentioned, four sampling periods were selected to bracket diurnal patterns in emissions and meteorology (Watson et al., 1998). Sampling periods 0500 to 1000, 1000 to 1600,and 1600 to 0000 are designed to capture fresh emission, while the sampling periods 1600 to 0000 and 0000 to 0500 correspond to the formation and tightening for the radiation inversion layer. January 4th, 2000 through January 7th, 2000 was the third episode of the four episodes and appears to be the most severe in Fresno. Data shown in this section are identified by DRI sample names. These sample names are defined

as the first two letters corresponding to the site name, the last two numbers of the year, two numbers corresponding to the month, two numbers corresponding to the day, and two numbers corresponding to the hour of the start sample collection. For example, FS01010400 indicates a sample that was collected at the Fresno site on January 4th beginning at midnight. In addition, analyte names are shortened in all figures and are defined in Appendix Table 5-1.

Figure 3-1 shows a high MW PAH variation that appears to correlate well with average traffic patterns. Vehicular emissions are assumed to be most abundant for the samples collected 0500 to 1000 and 1600 to 0000. However, an effect from the tightening of the inversion layer of the Fresno atmosphere can be seen in sample FS01010700. The high MW PAH shown in Figure 3-1 are found most abundantly in vehicular emissions (Zielinska et al., 2003).
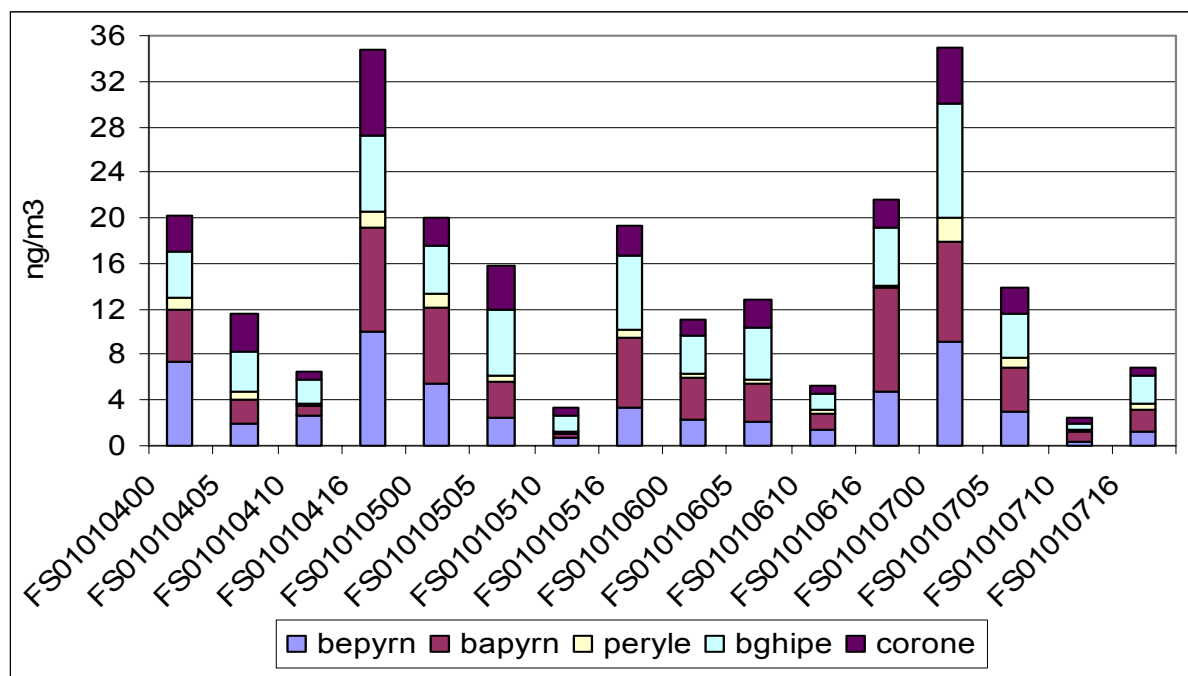
Figure 3-1. High MW PAH concentrations for Fresno site collected January 4th through January 7th.

Hopanes and steranes, oil biomarkers, are shown in Figure 3-2. The data shown here was very low in total concentration and does not correlate well to a traffic pattern or the meteorological conditions. These compounds are subject to many interferences even though the analytes were quantitated by selected ion monitoring, a GC/MS method. The interferences are greatest in biomass combustion emissions, due to high amounts of

unidentified resin acids and other similar unidentified compounds. These quantified interferences can be seen in recent data submitted for the source characterization portion of CRPAQS.
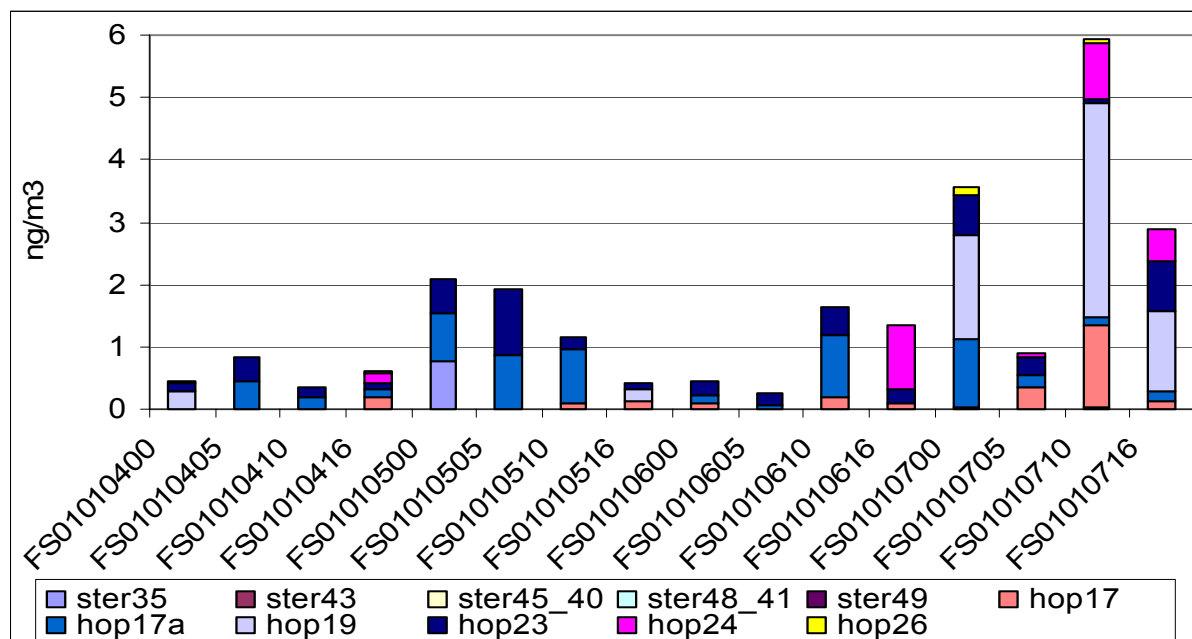

Figure 3-2. Hopane and Sterane concentrations for Fresno cite collected January 4th through January 7th.

Shown in Figure 3-3 are several branched alkanes. These compounds, norfarnesane, farnesane, norpristane, pristine, and phytane are biomarkers for petroleum products. The

distribution of these compounds in gasoline motor vehicle emissions compared to gasoline was reported by Schauer et al., (2002) to be quite similar. These compounds seem to correlate well with the traffic patterns with higher concentrations collected from 0500 to 1000 and 1600 to 0000.
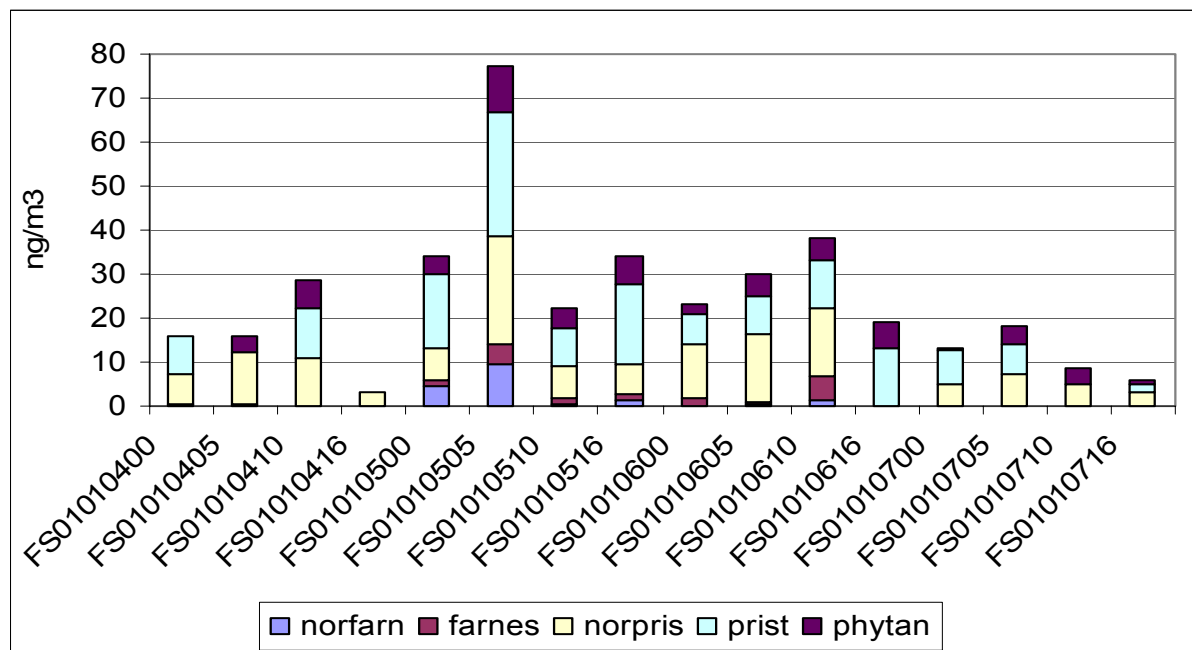

Figure 3-3. Branched Alkane concentrations for Fresno site collected January 4th through January 7th.

Shown in Figure 3-4 are the alkane-substituted cyclohexanes. These compounds range from C14 to C23 with substituted alkane groups ranging from C8 to C17. The results shown in Figure 3-4 are quite low in total concentration and do not appear to follow a pattern. It has been suggested by Schauer et al., (1999) that the cyclohexanes are useful for tracking diesel motor vehicle emissions.
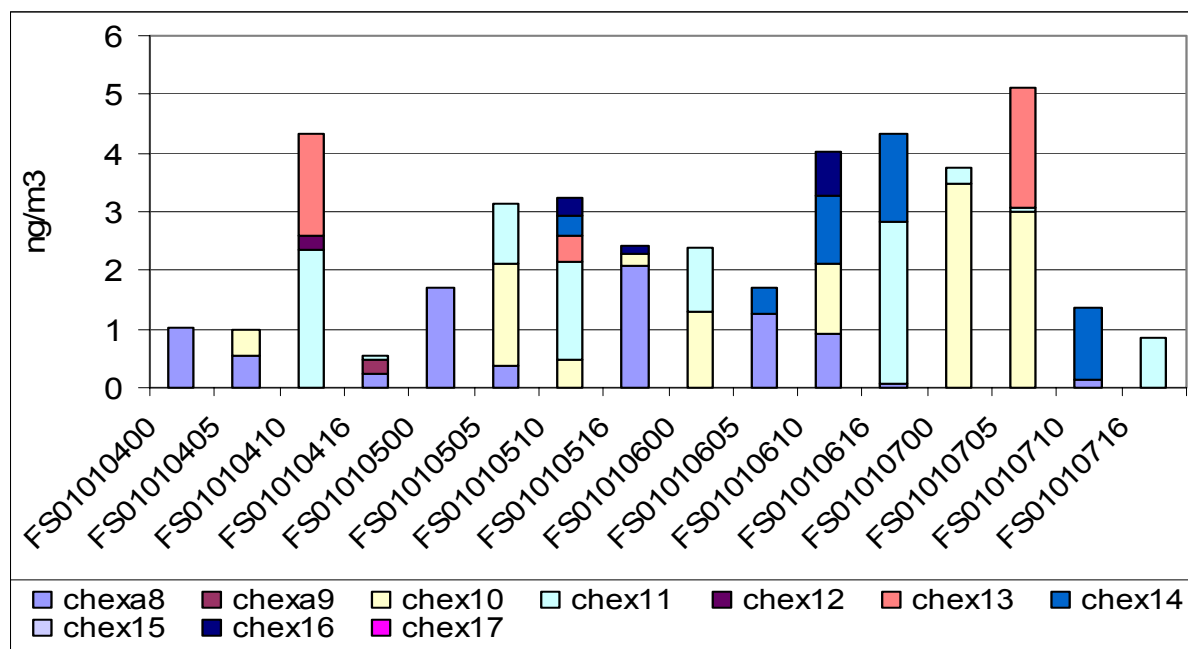

Figure 3-4. Alkane Substituted Cyclohexane concentrations for Fresno site collected January 4th through January 7th.

The methoxylated phenols and levoglucosan have been previously reported as unique semi-volatile compounds for biomass combustion (McDonald et al. 2000; Hawthorne et al. 1989; Simoneit et al., 1999) produced during the pyrolysis of wood lignin and cellulose, respectively. The two classes of methoxylated phenols found in wood smoke are guaiacols and syringols. Methoxylated phenol derivatives are produced in variable amounts between combustion of various species of wood. For example, syringols are only emitted from combustion of softwood, however guaiacols are emitted from both hard and soft woods. Shown in Figure 3-5 are the concentrations of methoxylated phenol derivatives. A pattern can be seen in the concentration variation for January 4th through January 7th for the Fresno site and may be explained by residential wood combustion. The highest concentrations were found for samples collected between 1600 and 0000 hours, which would correspond well with major residential patterns for home heating.
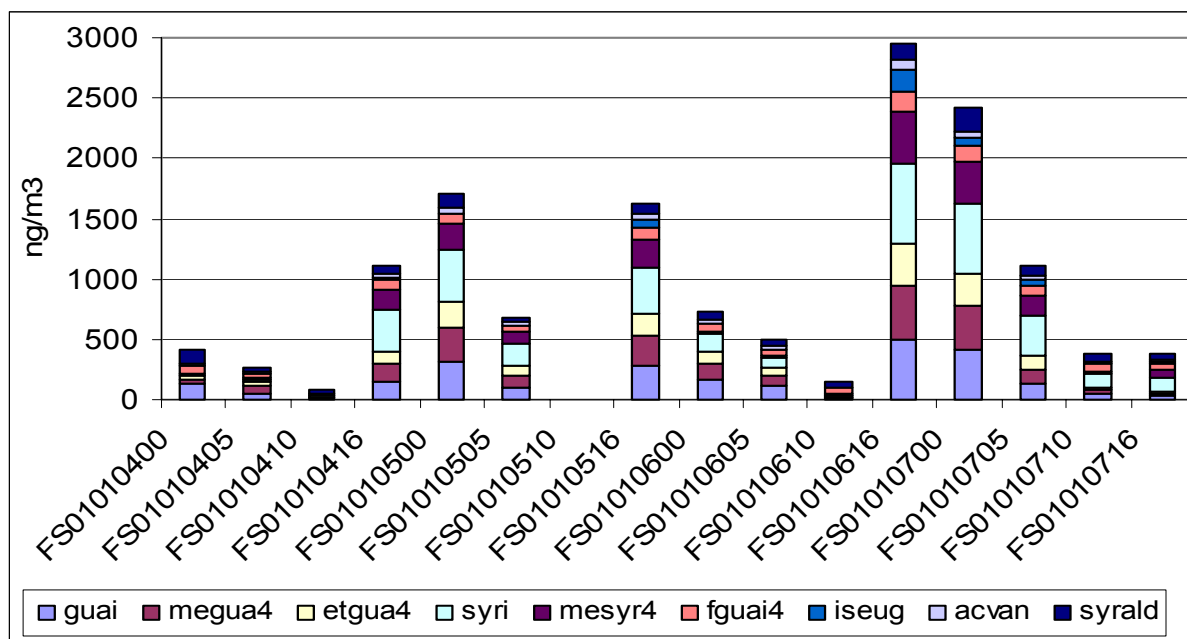
Figure 3-5. Methoxylated Phenol Derivative concentrations for Fresno site collected January 4th through January 7th.

Levoglucosan, a sugar anhydride, is formed in the pyrolysis of cellulose. The mechanism of pyrolysis was described by Simoneit et al.(1999). Levoglucosan concentrations are shown in Figure 3-6. For each of the episodic days shown below, the highest concentrations of levoglucosan occur between 0000 and 0500 hours. Levoglucosan is quite stable in the winter atmosphere and appears to vary in concentration as the meteorological conditions change. Although levoglucosan may be a useful tracer of residential wood combustion, it is important to note that the concentration of this single

organic constituent ranges from 80ng/m3 to 620 ng/m3 with an average concentration of approximately 300 ng/m3 for the samples collected between January 4th and January 7th. This may indicate that levoglucosan is very stable in the Fresno atmosphere and appears to be a good tracer of the overall contribution of residential wood combustion (Fraser and Lakshmanan 2000).
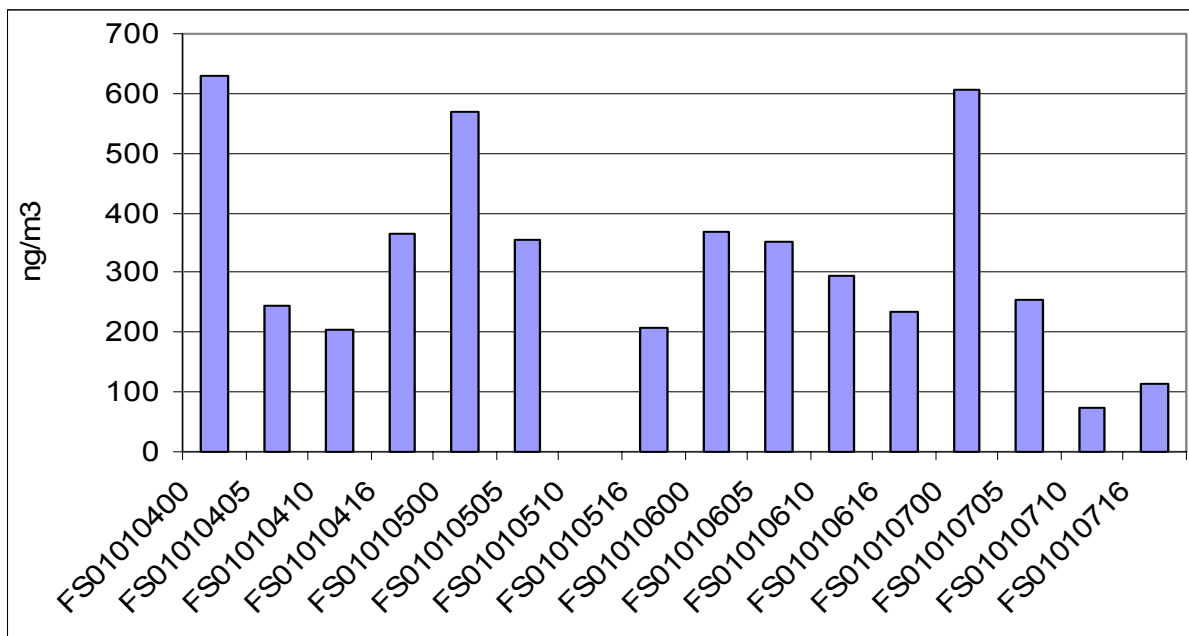
Figure 3-6. Levoglucosan concentrations for Fresno site collected January 4th through January 7th.

Although both methoxylated phenol derivatives and levoglucosan are derived from the combustion of wood, the variability of the concentrations of these compounds do not correlate well. Shown in Figure 3-7 is the correlation between the sum of the summed methoxylated phenol derivative concentration and the levoglucosan concentration. The difference between peaks and valleys of the summed methoxylated phenol concentration is quite high, however the difference is not very high in the concentrations of levoglucosan. This may be an indication of the stability of these compounds in the winter atmosphere. Methoxylated phenol derivatives have alkenoic character suggesting that these compounds are susceptible to oxidation by other atmospheric constituents in the presence of sunlight. These differences in reactivity/stability may explain the differences in the sample highs and lows in the Fresno site episode samples illustrated in Figure 3-7.
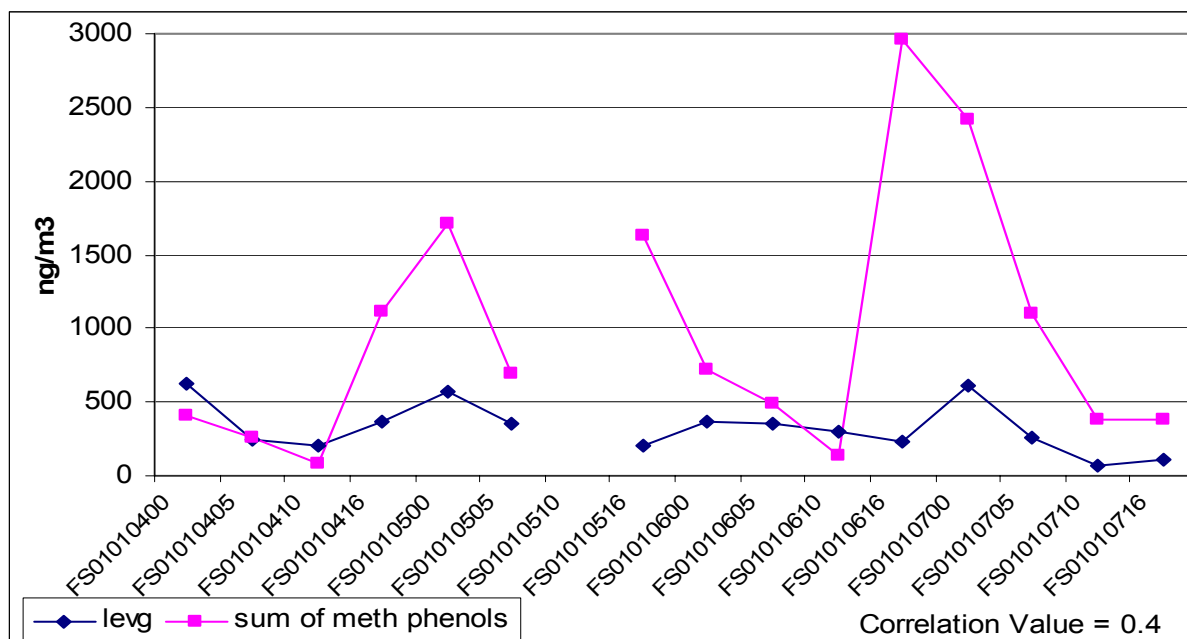
Figure 3-7. Sum of Methoxylated Phenol concentrations and Levoglucosan concentration for Fresno site collected January 4th through January 7th.

Semi-volatile organic compounds found in meat cooking are often also found in other sources and may be found in very low concentrations in the ambient atmosphere. Compounds such as cholesterol, palmitoleic acid, palmitic acid, stearic acid, and oleic acid are more abundant in meat cooking than in most other emission sources (Rogge et al., 1991). Several of the organic acids, which are indicative of meat cooking, are shown in Figure 3-8. FS01010416 and FS01010616 demonstrate a rising concentration of these organic acids,

which correlates well with expected food preparation times. Results from recent source sampling indicate the highest abundance is found in chicken and hamburger that has been charbroiled or propane grilled (Rinehart et al., 2003). Residential charbroiling and grilling of meats may not be common in the winter months. These cooking appliances may be more associated with summer activities and restaurant food preparation. The abundance of cholesterol in meat cooking source samples was found to be quite low compared to the abundance of palmitoleic and oleic acid in charbroiled chicken, charbroiled hamburger, and propane grilled chicken (Rinehart et al., 2003). Unfortunately, many of the cholesterol results were below method detection limits and thus cannot be employed to illustrate contributions from meat cooking emissions in these samples.

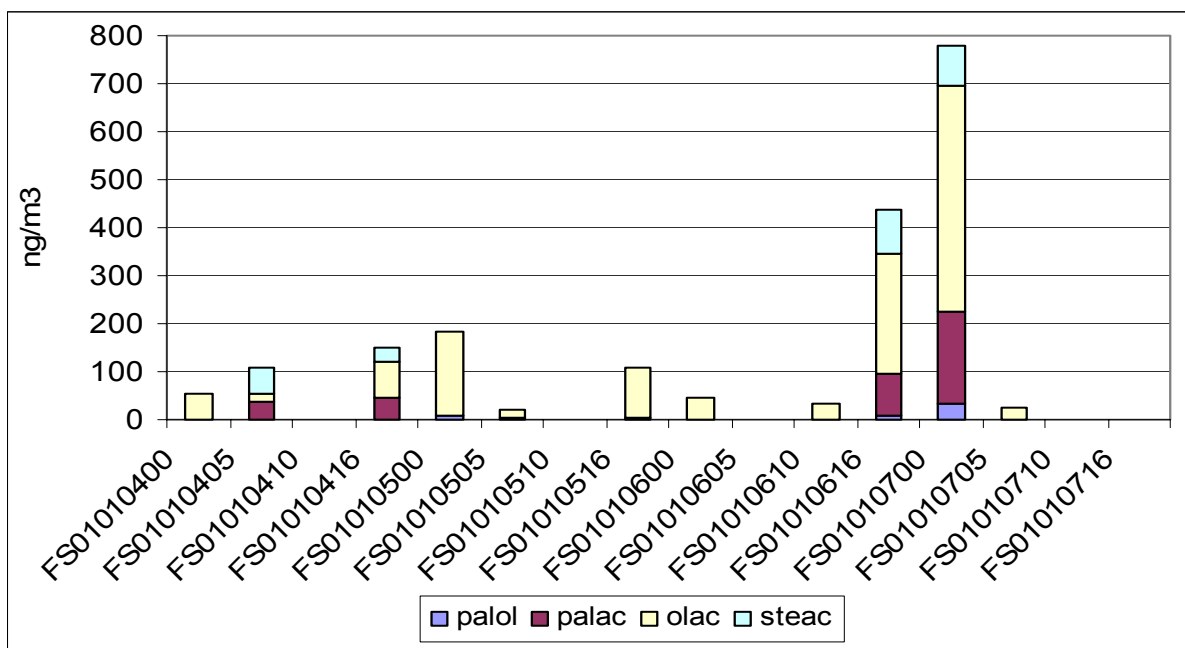**Figure 3-8.** Meat cooking organic acid concentrations for Fresno site collected January 4th through January 7th.

3.2   Tenax

Heavy hydrocarbons in the range of C_8 to C_{20} were collected during 15 episode days at the four anchor sites using Tenax-TA (Alltech) solid adsorbent. Each site is discussed individually in the following sections. The dates and times for sample collection are as

follows: 12/15/00-12/18/00, 12/26/00-12/28/00, 1/4/01-1/7/01, and 1/31/01-2/3/01 at 0000-0500, 0500-1000, 1000-1600 and 1600-2400 Pacific Standard Time each day. The anchor sites include Angiola, a non-urban setting, with a variety of surrounding agricultural activities; Bethel Inland, characterized as an interbasin transport site located in the Sacramento Delta area, in the transition area between the Bay Area and the San Joaquin Valley; Fresno, an urban site located in a residential/commercial area; and Auberry, the Sierra Foothills background site, is northeast of Fresno, at 637 m (2090 feet) above mean sea level.

3.2.1   Data Validation

To validate the data obtained from Tenax samples, measurements of selected compounds where compared to data collected using PUF/XAD. PUF/XAD samples were collected over a period of 12 hours, so the Tenax samples collected during the same period were averaged together.

Consistently high concentrations of every compound common to both methods in the Tenax sample collected at Angiola, CA on 12/16/00 at 1600 hours and 12/17/00 at 0000 hours are evidence of a much lower sampling volume than was recorded by the field operator. The Tenax sample collected at Angiola, CA on 1/4/01 at 1000 hours was unusually clean, with most compounds below the detection limit of the instrument. It is likely that there was a leak in the sampling apparatus during collection.

Figure 3-9 shows a correlation plot of 1,2,4-trimethyl benzene versus 1,2,3-trimethyl benzene for the data collected at the Bethel Island site, while Figure 3-10 shows a similar plot for 1-methyl naphthalene versus 2-methyl naphthalene. In both of these figures, the same three samples do not fit the overall correlation: the samples collected on 12/16/00 at 0000, 0500 and 1000 hours. When these samples are compared to their respective PUF/XAD samples (Figure 3-11), the agreement is poor (biased high). It is therefore likely that the flow rates were not measured correctly for these Tenax samples. (It should be noted that PUF/XAD samples show higher sensitivity to PAHs due to higher sampling volumes used for PUF/XAD collection.)

When comparing PUF/XAD data to Tenax data for the Fresno samples (in this data set the PUF/XAD samples were collected on the same schedule as the Tenax), three samples do not correlate due to a possible leak in the sampling apparatus for Tenax. These samples were collected on 12/28/00 at 0000 hours, 1/7/01 at 0500 hours and 2/2/01 at 1600 hours. In these samples, the values determined by the Tenax method are near or below the detection limit.

Within the data set of Tenax samples collected at the Sierra Nevada Foothills site, the highest measured values of *n*-eicosane and *n*-nonadecane occur in a field blank taken on 12/16/00. It is likely that these values are due to co-eluting compounds since these long straight chain alkanes are not commonly found in unsampled Tenax at high values. In addition, these samples were analyzed by flame ionization detection (FID), which does not provide spectral analysis. A high concentration of 1,2,3,4-tetramethyl benzene was measured

in a back-up Tenax sample collected on 02/03/01 at 0500 hours at the Sierra Nevada Foothills site. This is likely due to the co-elution of another unidentified compound.

Table 3-1 lists the Tenax samples that are invalid for the CRPAQS Heavy Hydrocarbon Field Study. The two reasons for the exclusion of these samples from the database stem from errors during sampling, e.g. leaks in the sampling apparatus and incorrect flow rate measurements.

Table 3-1. Invalid Tenax samples.

Site	Date and Time	Reason for Invalidation of Sample
Angiola	12/16/00 at 1600 hours	Measured sampling volume too high
	12/17/00 at 0000 hours	Measured sampling volume too high
	1/4/01 at 1000 hours	Leak in sampling apparatus
Bethel Island	12/16/00 at 0000 hours	Measured sampling volume too high
	12/16/00 at 0500 hours	Measured sampling volume too high
	12/16/00 at 1000 hours	Measured sampling volume too high
Fresno	12/28/00 at 0000 hours	Leak in sampling apparatus
	1/7/01 at 0500 hours	Leak in sampling apparatus
	2/2/01 at 1600 hours	Leak in sampling apparatus

3.2.2   Evaluation of Data

Figure 3-12 illustrates the concentrations of ethyl benzene (found in automobile exhaust) and cyclohexanone (a compound formed in situ in the atmosphere from the oxidation of cyclohexane (Orlando et al., 2000) with a lifetime of 43.5 hours (Albaladejo et al., 2003)) at Angiola, while Figure 3-13 shows the same time series at Bethel Island. Samples collected on 12/16/00 at 0000 and 0500 hours at Bethel Island were removed due to data validation concerns expressed in the above section. Figures 3-14 and 3-15 show concentrations for these compounds for the Fresno and Sierra Nevada Foothills sites, respectively. These figures show that ethyl benzene is out of phase with cyclohexanone. Ethyl benzene concentrations generally peak in the morning hours, while cyclohexanone concentrations usually peak during the second half of the day, indicating that fresh emission often dominate in the morning, while aging air masses prevail during the latter part of the day.

For many VOCs in the polluted atmosphere, reaction with the hydroxyl radical (HO) is the major degradation pathway. Atmospheric lifetimes of VOCs are generally calculated according to their rate of reaction with HO. Compounds which share common sources will maintain their relative abundances when freshly emitted, but will change in proportion to each other as the air mass containing them ages. Ethyl benzene and 1,3,5-trimethylbenzene have atmospheric lifetimes of 7.82 and 0.97 hours, respectively. Their ratios are plotted in a time series in Figure 3-16 for the four anchor sites, showing a diurnal variation in which fresh emissions in the morning were followed by photochemical aging during the afternoon and evening hours. The ratio of these compounds is at its lowest at the Sierra Nevada

Foothills site, indicating that the air mass sampled at this site is often aged the longest of all the sites with no sources of 1,3,5-trimethylbenzene near by. Figure 3-17 shows the ratio of cyclohexanone to ethyl benzene for the four anchor sites. For the cases of Bethel Island and Sierra Nevada Foothills, there are instances were the ratio is significantly higher than the remaining sampling days. This may indicate that an aged air mass moved into the area for a short time (approximately 24 hours for Bethel Island, less than a day for Sierra Nevada Foothills).
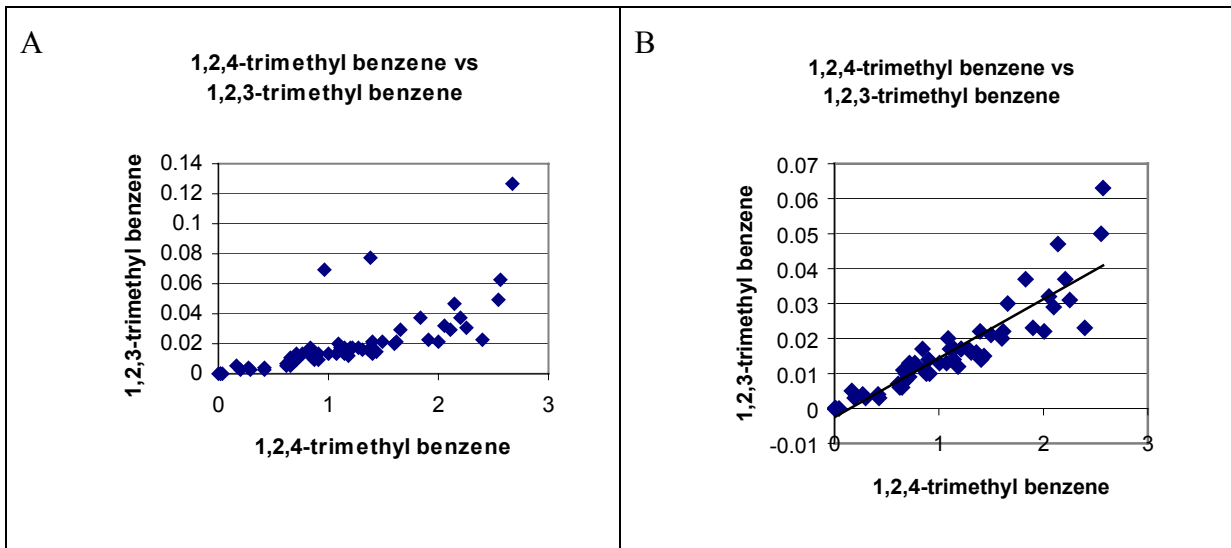

Figure 3-9. Correlation plot of 1,2,4-trimethyl benzene versus 1,2,3-trimethyl benzene for the data collected at the Bethel Island site, with outliers (Panel A) and without (Panel B).
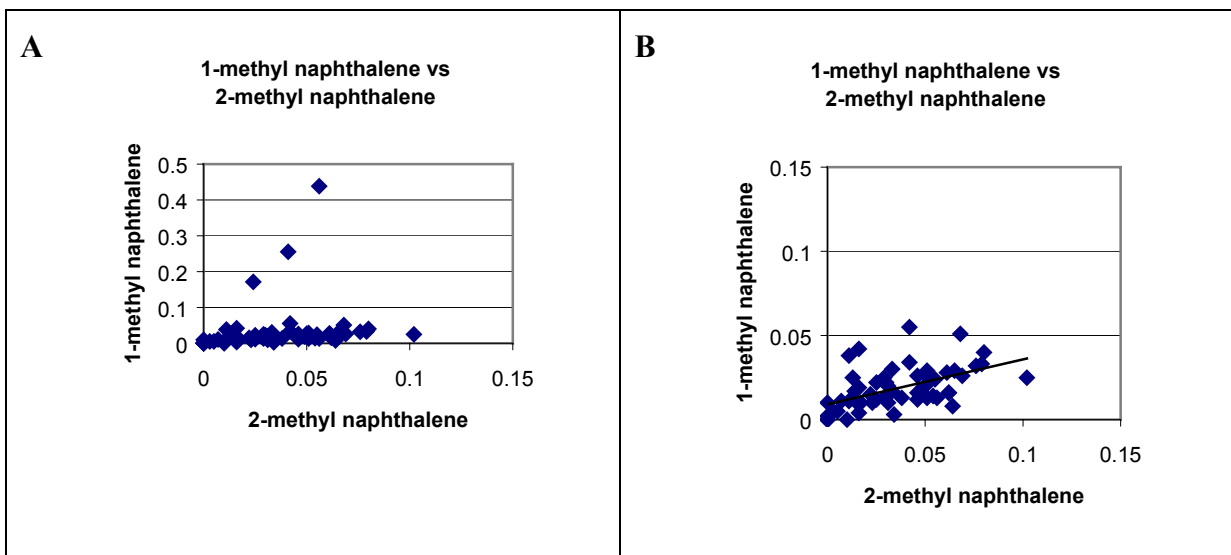
Figure 3-10. Correlation plot for 1-methyl naphthalene versus 2-methyl naphthalene for the Bethel Island site, with outliers (Panel A) and without (Panel B).
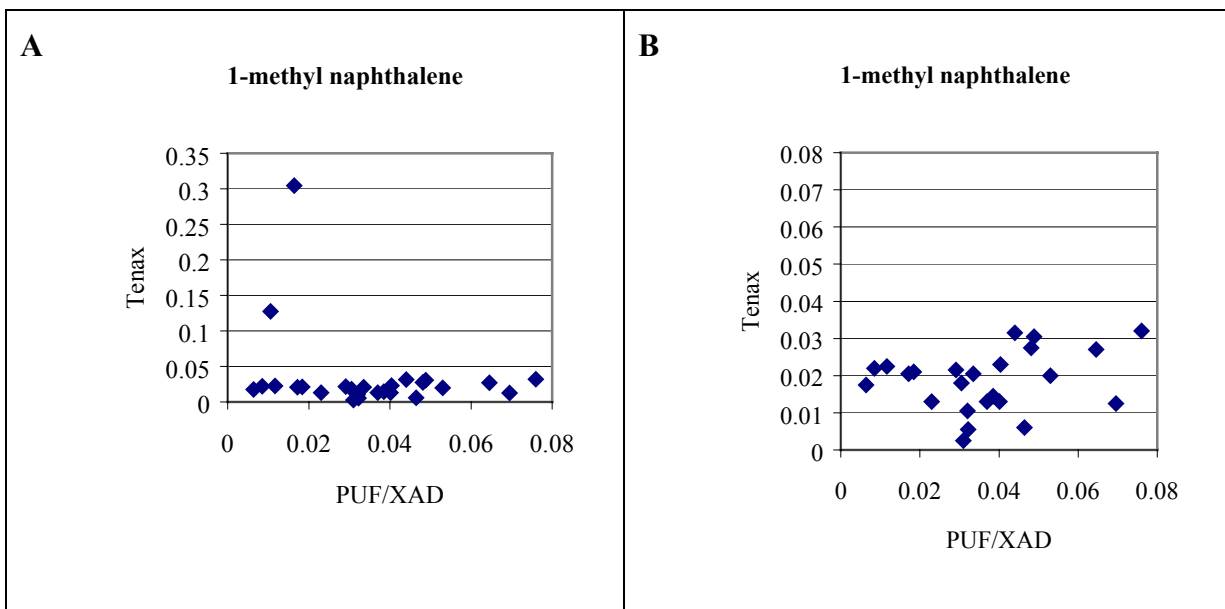
Figure 3-11. Comparison of 1-methyl naphthalene for PUF/XAD versus Tenax samples for data collected at Bethel Island, with outliers (Panel A) and without (Panel B). It should be noted that PUF/XAD samples show higher sensitivity to PAHs due to higher sampling volumes.

Figure 3-12. Concentrations of ethyl benzene and cyclohexanone at Angiola.
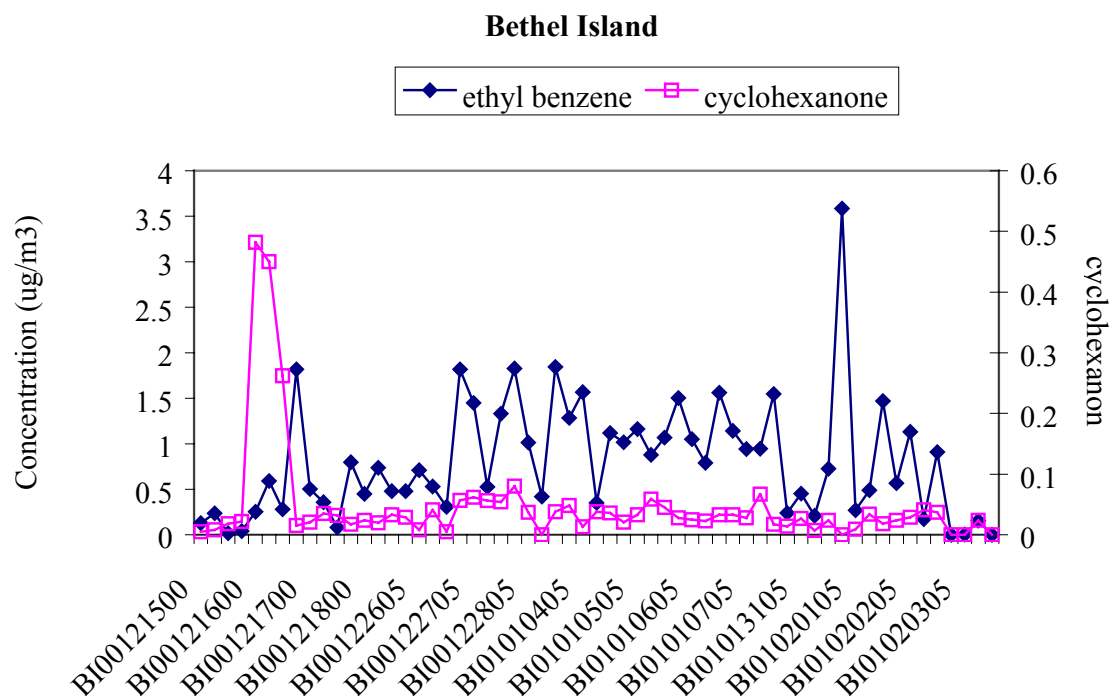
Figure 3-13. Concentrations of ethyl benzene and cyclohexanone at Bethel Island.
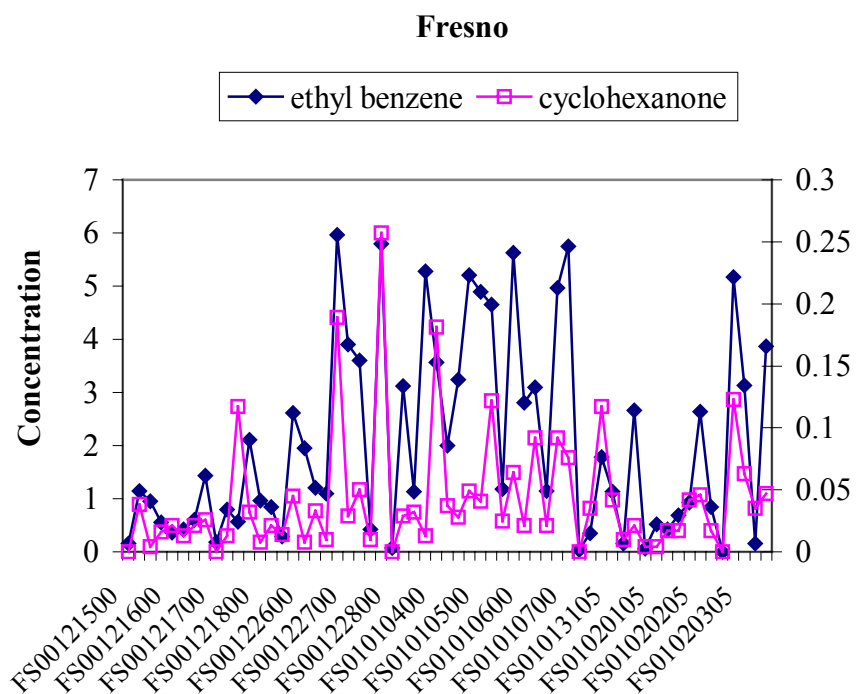
Figure 3-14. Concentrations of ethyl benzene and cyclohexanone at Fresno.

3-19
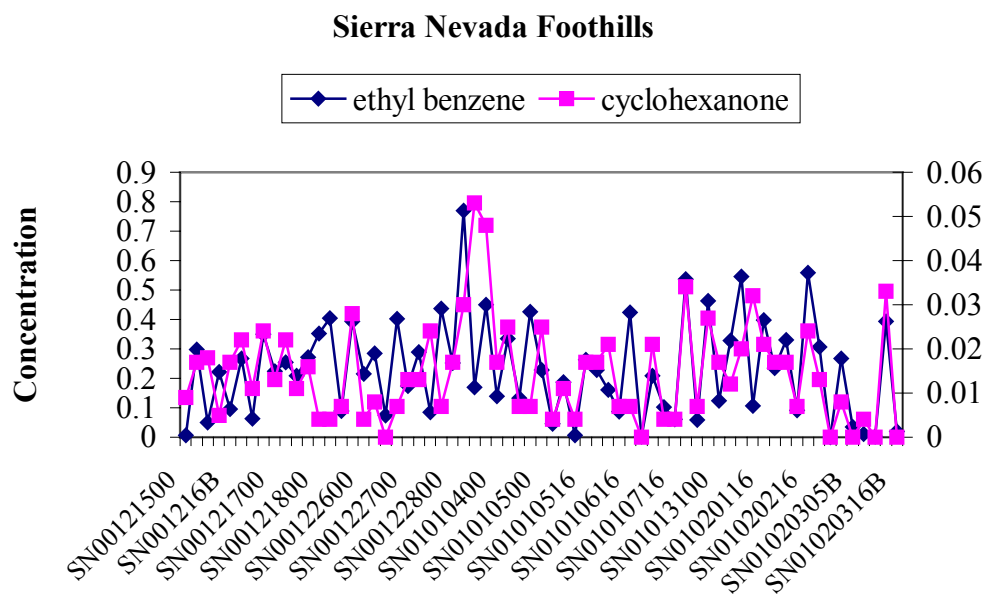
Figure 3-15. Concentrations of ethyl benzene and cyclohexanone at Sierra Nevada Foothills.

B

Ratio of 1,3,5-trimethyl benzene to ethyl benzene at Angiola
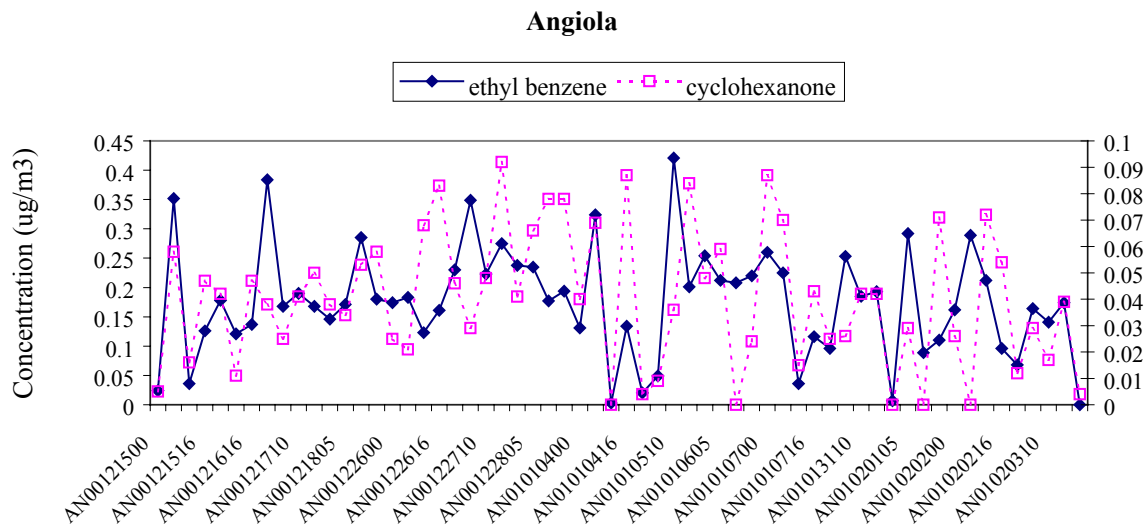
Ratio of 1,3,5-trimethyl benzene to ethyl benzene at Bethel Island

C

Ratio of 1,3,5-trimethyl benzene to ethyl benzene at Fresno

Ratio of 1,3,5-trimethyl benzene to ethyl benzene at Sierra Nevada Foothills

Figure 3-16. The ratio of 1,3,5-trimethylbenzene to ethyl benzene in a time series for all four anchor sites: Panel A – Angiola, Panel B – Bethel Island, Panel C – Fresno, and Panel D – Sierra Nevada Foothills.

B

**Ratio of cyclohexanone
to ethyl benzene at Angiola**

**Ratio of cyclohexanone
to ethyl benzene at Bethel Island**

C   **Ratio of cyclohexanone to ethyl benzene at Fresno**

Ratio of cyclohexanone to ethyl benzene at Sierra Nevada Foothills

Figure 3-17. The ratio of cyclohexanone to ethyl benzene in a time series for all four anchor sites: Panel A – Angiola, Panel B – Bethel Island, Panel C – Fresno, and Panel D – Sierra Nevada Foothills..
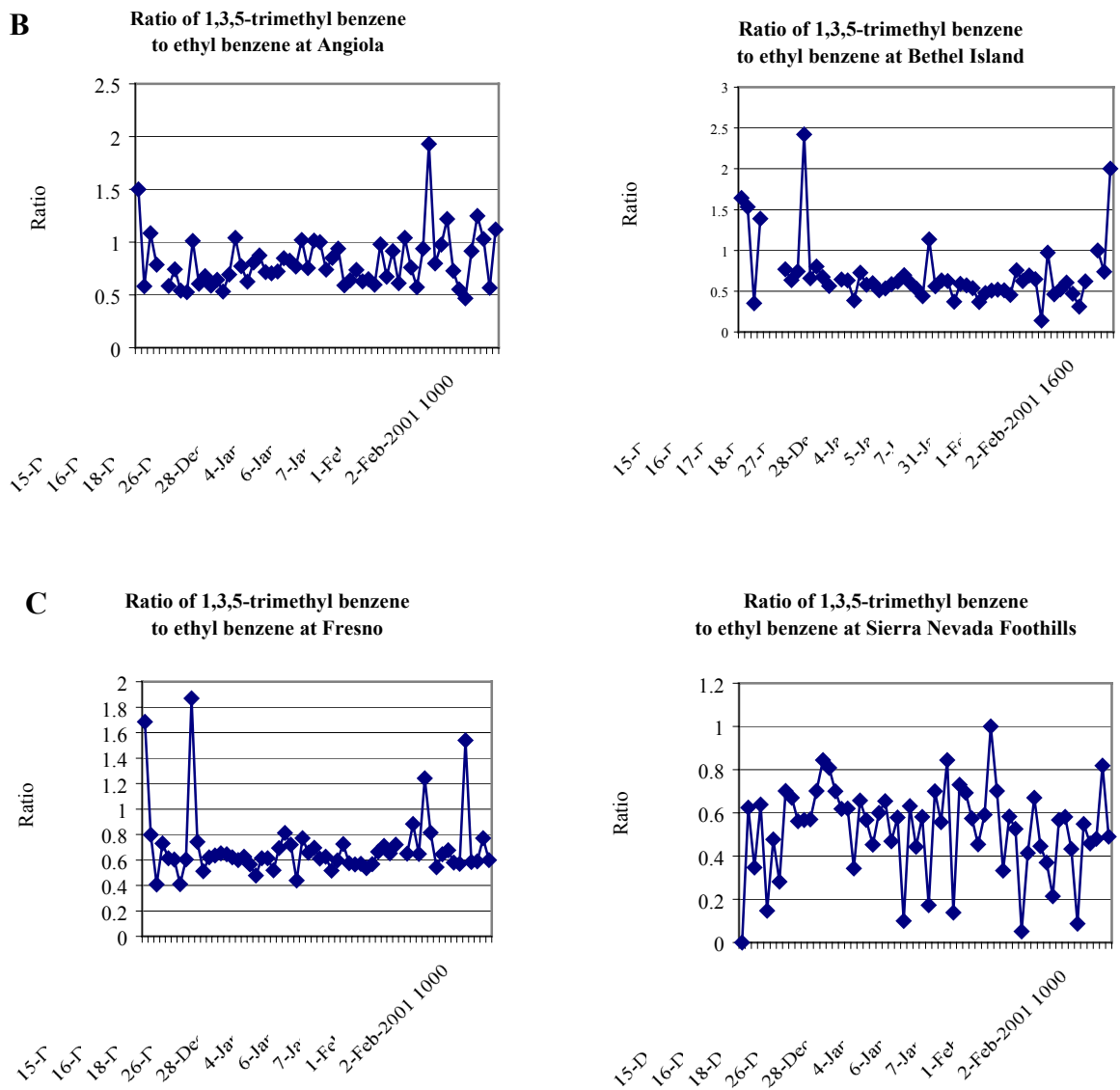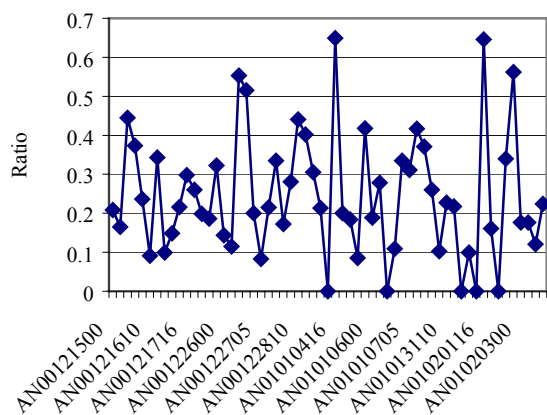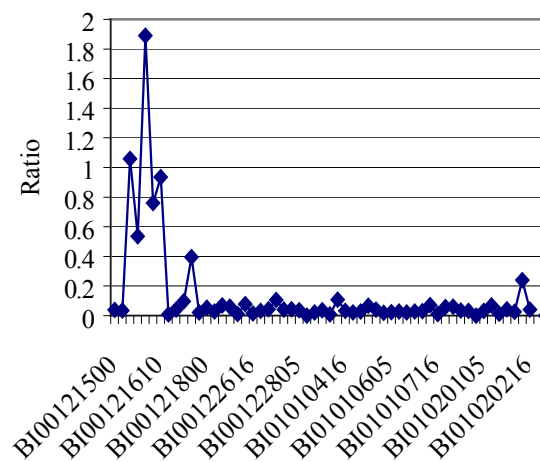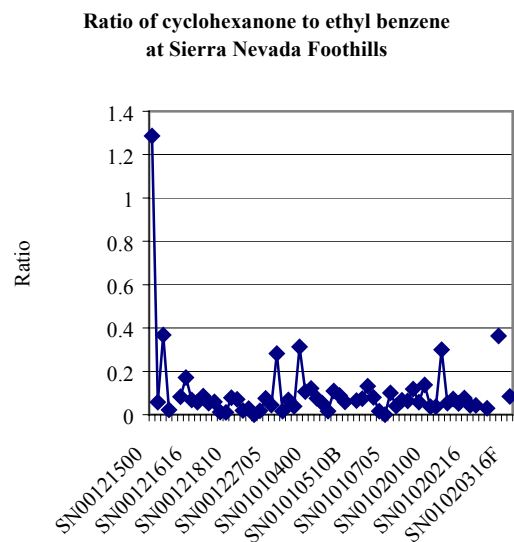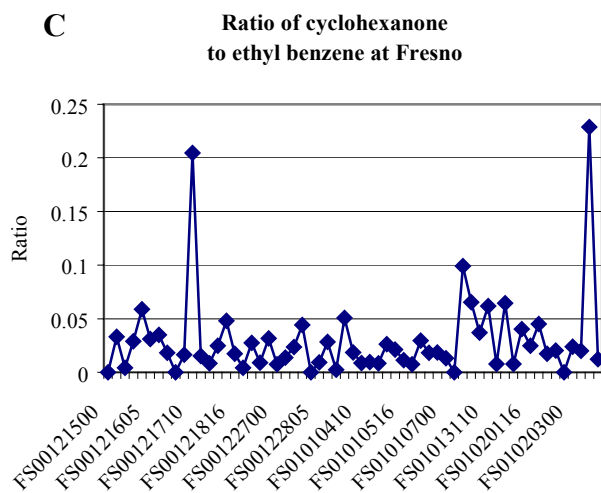
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5.   APPENDIX

Table 5-1. List of Semi-Volatile Organic Compounds and mnemonics.

Polycyclic Aromatic Hydrocarbons	
NAPHTH	Naphthalene
MNAPH2	2-methylnaphthalene
MNAPH1	1-methylnaphthalene
BIPHEN	Biphenyl
M_2BPH	2-Methylbiphenyl
ENAP12	1+2ethylnaphthalene
DMN267	2,6+2,7-dimethylnaphthalene
DM1367	1,3+1,6+1,7dimethylnaphth
D14523	1,4+1,5+2,3-dimethylnaphth
ACNAPY	Acenaphthylene
DMN12	1,2-dimethylnaphthalene
M_3BPH	3-Methylbiphenyl
ACNAPE	Acenaphthene
M_4BPH	4-Methylbiphenyl
DBZFRN	Dibenzofuran
ATMNAP	A-trimethylnaphthalene
BTMNAP	B-trimethylnaphthalene
CTMNAP	C-trimethylnaphthalene
ETMNAP	E-Trimethylnaphthalene
FTMNAP	F-trimethylnaphthalene
TMI235N	2,3,5+I-trimethylnaphthalene
JTMNAPu	J-trimethylnaphthalene
TM245N	2,4,5,-trimethylnaphthalene
FLUORE	Fluorene
TM145N	1,4,5-trimethylnaphthalene
A_MFLU	A-methylfluorene
M_1FLU	1-methylfluorene
B_MFLU	B-methylfluorene
FL9ONE	9-fluorenone
PHENAN	Phenanthrene
ANTHRA	Anthracene
XANONE	Xanthone
ACQUONE	Acenaphthenequinone
A_MPHT	A-methylphenanthrene
M_2PHT	2-methylphenanthrene
PNAPONE	Perinaphthenone
B_MPHT	B-methylphenanthrene
C_MPHT	C-methylphenanthrene
M_1PHT	1-methylphenanthrene
ANTHRN	Anthrone
M_9ANT	9-methylanthracene

Polycyclic Aromatic Hydrocarbons

ANRQUONE	Anthraquinone
DM36PH	3,6-dimethylphenanthrene
A_DMPH	A-dimethylphenanthrene
B_DMPH	B-dimethylphenanthrene
C_DMPH	C-dimethylphenanthrene
D_DMPH	D-dimethylphenanthrene
E_DMPH	E-dimethylphenanthrene
FLUORA	Fluoranthene
C1MFLPY	1-MeFl+C-MeFl/Py
PYRENE	Pyrene
ANTAL9	9-Anthraaldehyde
RETENE	Retene
BMPYFL	B-MePy/MeFl
CMPYFL	C-MePy/MeFl
DMPYFL	D-MePy/MeFl
M_4PYR	4-methylpyrene
M_1PYR	1-methylpyrene
BZFLO23	2,3-Benzofluorene
BNTIOP	Benzonaphthothiophene
BZCPHEN	Benzo(c)phenanthrene
BAANTH	Benz(a)anthracene
CHRYSN	Chrysene
BZANTHR	Benzanthrone
BAA7_12	Benz(a)anthracene-7,12-dione
CHRY56M	5+6-methylchrysene
M_7BAA	7-methylbenz(a)anthracene
CHRYQ14	1,4-chrysenequinone
BBJKFL	Benzo(b+j+k)fluoranthene
BEPYRN	BeP
BAPYRN	BaP
PERYLE	Perylene
M_7BPY	7-methylbenzo(a)pyrene
DBAPONE	9,10-dihyrobenzo(a)pyrene-7(8H)-one
INCDPY	Indeno[123-cd]pyrene
DBANTH	Dibenzo(ah+ac)anthracene
BGHIPE	Benzo(ghi)perylene
CORONE	Coronene

Steranes & Hopanes

STER35	C27-20S-13ß(H),17a(H)-diasterane
STER43	C27-20R5a(H),14ß(H)-cholestane
STER45_40	C27-20R5a(H),14a(H),17a(H)-cholestane&C29-20S13ß(H),17a(H)-diasterane
STER48	C28-20S5a(H),14ß(H),17ß(H)-ergostane&C29-20R-13a(H),17ß(H)-diasterane
STER49	C28-20R5a(H),14a(H),17a(H)-ergostane

Polycyclic Aromatic Hydrocarbons

HOP17	17a(H),21ß(H)-30-Norhopane
HOP17a	17β(H),21a(H)-30-norhopane
HOP19	17a(H),21ß(H)-Hopane
HOP23	17ß(H),21ß(H)-Hopane
HOP24	22S-17a(H),21ß(H)-30,31-Bishomohopane
HOP26	22S-17a(H),21ß(H)-30,31,32-Trishomohopane

Polar Organics

HEXAC	hexanoic acid (c6)
HEPTAC	heptanoic acid (c7)
MEMALON	me-malonic (d-c3)
GUAI	guaiacol
BENAC	benzoic acid
OCTANAC	octanoic acid (c8)
GLYCERO	glycerol
MALEAC	maleic acid
SUCAC	succinic acid (d-c4)
MEGUA4	4-me-guaiacol
MESUCAC	me-succinic acid (d-c4)
OTOLUIC	o-toluic
PICAC	picolinic acid
MTOLUIC	m-toluic
NONAC	nonanoic acid (c9)
PTOLUIC	p-toluic
MEPIC36	3-, 6-methylpicolinic acid
DIMEB26	2,6-dimethylbenzoic acid
ETGUA4	4-ethyl-guaiacol
SYRI	syringol
GLUAC	glutaric acid (d-c5)
MEGLU2	2-methylglutaric (d-c5)
DIMEB25	2,5-dimethylbenzoic acid
MEGLU3	3-methylglutaric acid (d-c5)
DIMEB24	2,4-dimethylbenzoic acid
DIMEB35	3,5-dimethylbenzoic acid
DIMEB23	2,3-dimethylbenzoic acid
DECAC	decanoic acid (c10)
ALGUAI4	4-allyl-guaiacol (eugeenol)
MESYR4	4-methyl-syringol
DIMEB34	3,4-dimethylbenzoic acid
HEXDAC	hexanedioic (adipic) acid (d-c6)
TDECEN2	trans-2-decenoic acid
CPINAC	cis-pinonic acid
MEADIP3	3-methyladipic acid (d-c6)
FGUAI4	4-formyl-guaiacol (vanillin)

Polycyclic Aromatic Hydrocarbons

UNDEC	undecanoic acid (c11)
ISEUG	isoeugenol
HEPDAC	heptanedioic (pimelic) acid (d-c7)
ACVAN	acetovanillone
LAUAC	dodecanoic (lauric) acid (c12)
PHTHAC	phthalic acid
LEVG	levoglucosan
SYRALD	syringaldehyde
TDECAC	tridecanoic acid (c13)
ISPHAC	isophthalic acid
AZEAC	azelaic acid (d-c9)
MYROL	myristoleic acid
MYRAC	myristic acid (c14)
SEBAC	sebacic acid (d-c10)
PDECAC	pentadecanoic acid (c15)
UNDECDI	undecanedioic acid (d-c11)
PALOL	palmitoleic acid
PALAC	palmitic acid (c16)
ISSTER	isostearic acid
HEPTDC	heptadecanoic acid (c17)
UNDD111	1,11-undecanedicarboxylic acid (d-c13)
OLAC	oleic acid
ELAC	elaidic acid
STEAC	stearic acid (c18)
DODD112	1,12-dodceanedicarboxylic acid (d-c14)
NDECAC	nonadecanoic acid (c19)
DHABAC	dehydroabietic acid
ECOSAC	eicosanoic acid (c20)
ABAC	abietic acid
HCOSAC	heneicosanoic acid (c21)
CHOL	cholesterol
BSIT	b-sitosterol

High MW Alkanes

NORFARN	norfarnesane
A3MHEX	a-3-methyl-1-hexylcyclohexane
A4MHEX	a-4-methyl-1-hexylcyclohexane
A2MHEX	a-2-methyl1-hexylcyclohexane
B3MHEX	b-3-methyl-1-hexylcyclohexane
B4MHEX	b-4-methyl-1-hexylcyclohexane
B2MHEX	b-2-methyl1-hexylcyclohexane
CHEXA7	heptylcyclohexane
FARNES	farnesane
CHEXA8	octylcyclohexane

Polycyclic Aromatic Hydrocarbons

CHEXA9	Nonylcyclohexane
NORPRIS	norpristane
HEXADE	hexadecane
HEPTAD	heptadecane
CHEX10	decylcyclohexane
PRIST	pristane
CHEX11	undecylcyclohexane
OCTAD	octadecane
NONAD	nonadecane
PHYTAN	phytane
CHEX12	dodecylcyclohexane
CHEX13	tridecylcyclohexane
CHEX14	tetradecylcyclohexane
EICOSA	eicosane
HENEIC	heneicosane
CHEX15	pentadecylcyclohexane
CHEX16	hexadecylcyclohexane
TRICOSA	triacosane
CHEX17	heptadecylcyclohexane
CHEX18	octadecylcyclohexane
COSAN4	tetracosane
COSAN5	pentacosane
COSAN6	hexacosane
CHEX19	nonadecylcyclohexane
CHEX20	eicosylcyclohexane
COSAN7	heptacosane
COSAN8	octacosane
COSAN9	nonacosane
CONTAN	triacontane
CONTAN1	hentriacontane
CONTAN2	dotriacontane
CONTAN3	tritriacontane
CONTAN4	tetratriacontane
CONTAN5	pentatriacontane
CONTAN6	hexatriacontane

Table 5-2. Heavy Hydrocarbons measured with Tenax and their mnemonics.

Mnemonic	Name
ETBZ	ethylbenzene
MEOCT2	2-methyl octane
MP_XYL	m&p-xylene
MEOCT	3-methyloctane
CYHEONE	cyclohexanone
HEPTONE	2-heptanone
STYR	styrene
O_XYL	o-xylene
NONE1	1-nonene
N_NON	n-nonane
IPRBZ	isopropylbenzene
PRCYHEX	propylcyclohexane
DMOCT	dimethyloctane
A_PINE	a-pinene
N_PRBZ	n-propylbenzene
BZALDE	benzaldehyde
M_ETOL	m-ethyltoluene
P_ETOL	p-ethyltoluene
BZ135M	1,3,5-trimethylbenzene
O_ETOL	o-ethyltoluene
B_PINE	b-pinene
BZ124M	1,2,4-trimethylbenzene+1-dec
MESTYR	4-methylstyrene
N_DEC	n-decane
I_BUBZ	iso-butylbenzene
BZ123M	1,2,3-trimethylbenzene
M_IPRTOL	m-isopropyltoluene
P_IPRTOL	p-isopropyltoluene
LIMON	limonene
INDAN	indan
O_IPRTOL	o-isopropyltoluene
INDENE	indene
DEBZ13	1,3-diethylbenzene
C4BZA2	1,4-diethylbenzene+Tenax-Bgr
TOLALD	tolualdehyde+5-ethyl-m-xylen
DMETBZ	dimethylethylbenzene
DEBZ12	1,2-diethylbenzene
TOL2PR	2-n-propyltoluene
P_XYLET2	2-ethyl-p-xylene
O_XYLET4	4-ethyl-o-xylene

Mnemonic	Name
NONAL	nonanal+1-undecene
N_UNDE	n-undecane
IPRXYL_5	5-isopropyl-m-xylene
BZ1245	1,2,4,5-tetramethylbenzene
BZ1235	1,2,3,5-tetramethylbenzene
IND_2M	2-methylindan
IND_1M	1-methylindan
BZ1234	1,2,3,4-tetramethylbenzene
C5BZ_3	pentylbenzene
THNAPH	1,2,3,4-tetrahydronaphthalen
DHNAPH	1,2-dihydronaphthalene
DIPRB_14	1,4-diisopropylbenzene
DECONE2	2-decanone
NAPHTH	naphthalene
DECAL	decanal+1-dodecene
N_DODE	n-dodecane
PMEBZ	pentamethylbenzene
N_TRID	n-tridecane
NAP_2M	2-methylnaphthalene
NAP_1M	1-methylnaphthalene
BPHENA	biphenyl
N_TETD	n-tetradecane
NAP2ET	1+2-ethylnaphthalene
DMN26	2,6-+2,7-dimethylnaphthalene
DMN13	1,6-+1,3+1,7dimethylnaphthal
ACENAP	acenaphthylene
DMN14	2,3+1,5+1,4-dimethylnaphthal
DMN12	1,2-dimethylnaphthalene
ACENPE	acenaphthene
N_PEND	n-pentadecane
FLUORE	fluorene
N_HEXD	n-hexadecane
N_HEPD	n-heptadecane
N_OCTD	n-octadecane
PHENA	phenanthrene
N_NOND	n-nonadecane
N_EICO	n-eicosane
TIDNMHC	total identified nmhc
TUNID	total unidentified nmhc
T_BKG	total background
TIDOTHR	total identified other

Agricultural Sites
- A-1: Angiola: ANGI
- A-2: Helm-Central Fresno Co.: HELM
- A-3: Pixley Wildlife Refuge: PIXL
- A-4: Agricultural Feedlot/Dairy: FEDL

Residential Sites
- R-1: Fresno/First St.: FRS
- R-2: Bakersfield: BAC
- R-3: San Jose: SJ4
- R-4: Bethel Island: BTI
- R-5: Sacramento/DPM: SDP

Industrial Sites
- I-1: Fresno/First St.: FSF
- I-2: Sacramento/T St.: S13
- I-3: Fellows: FEL
- I-4: Corcoran: COP
- I-5: Modesto: M14

Background Sites
- B-1: Sierra Nevada Foothills: SNF
- B-2: Olancha: OCW
- B-3: Yosemite National Park: YOSE
- B-4: Edwards AFB: EDW
- B-5: China Lake NAWC: CHL
- B-6: Livermore: LVR
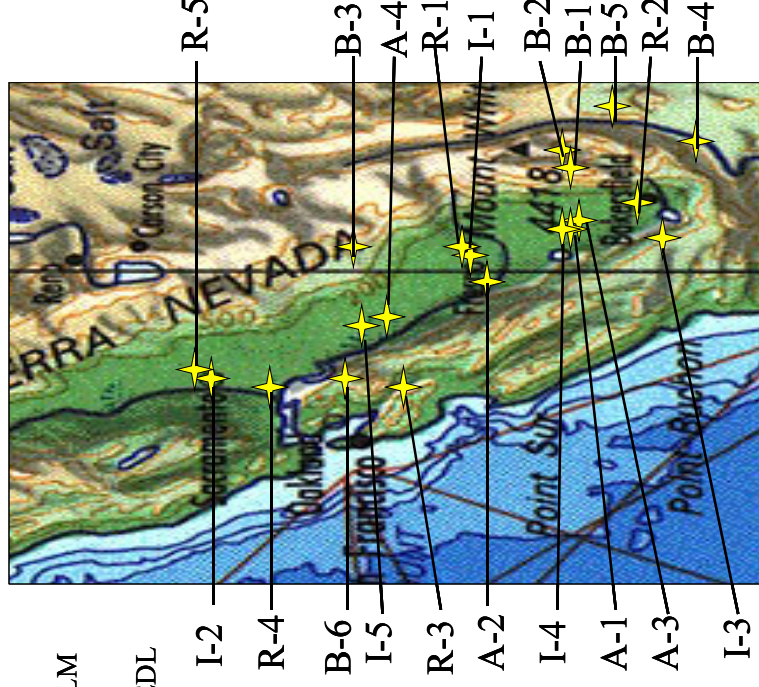
Figure 5-1. Annual Average Satellite sites with mnemonics.
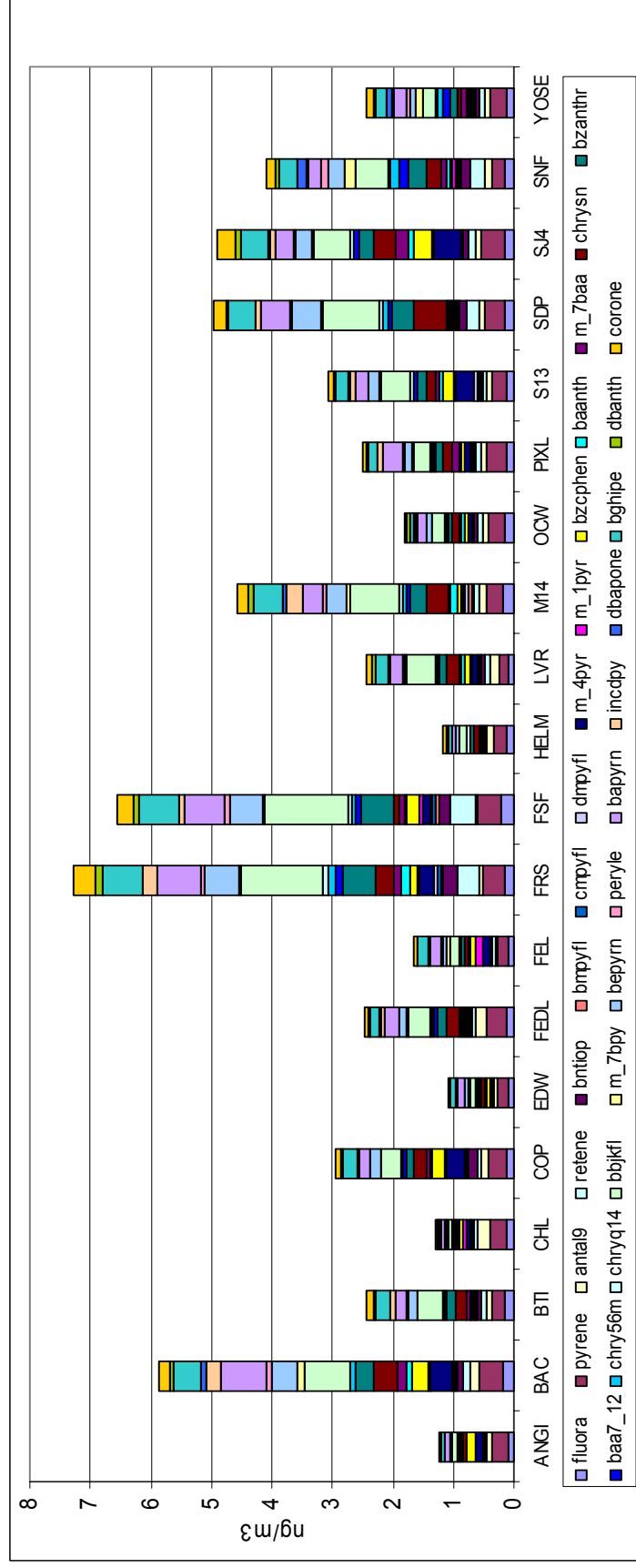
Figure 5-2. High MW PAH Annual Average concentrations for the 20 Satellite sites.

5-10
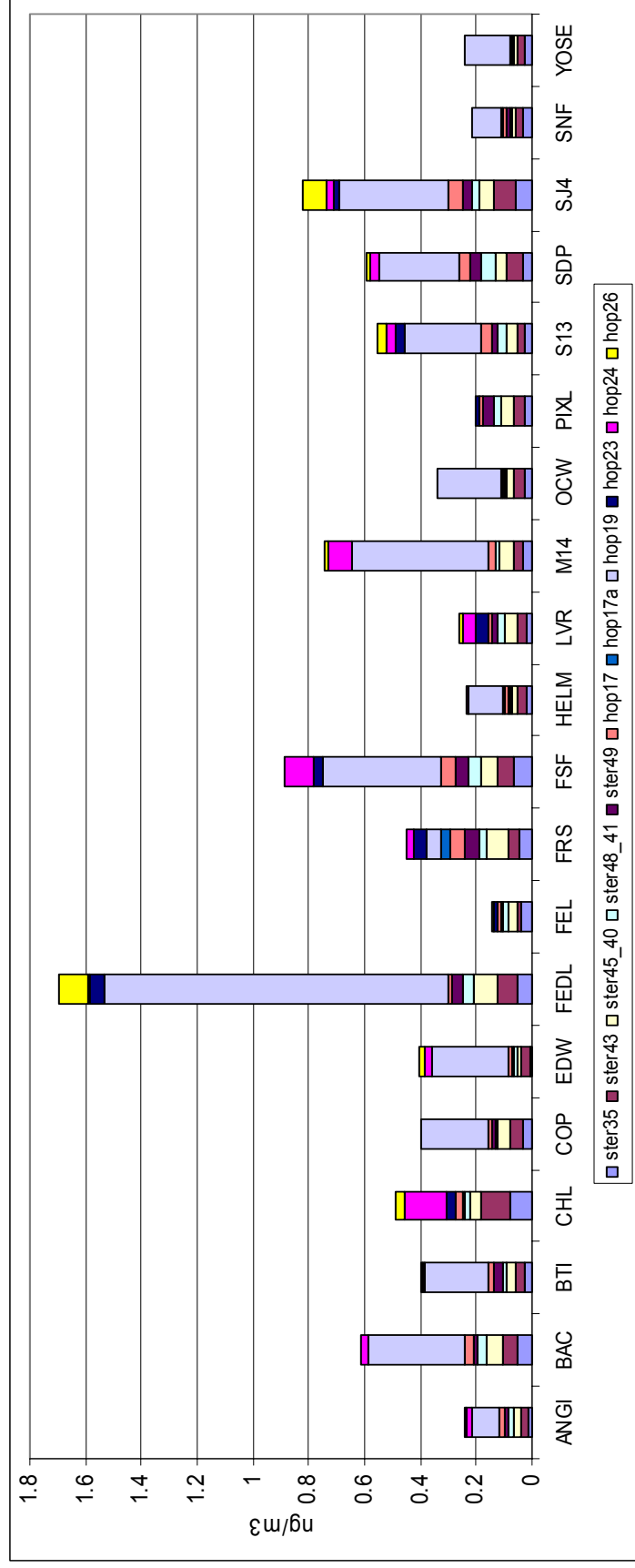
Figure 5-3. Sterane and Hopane Annual Average concentrations for the 20 Satellite sites.
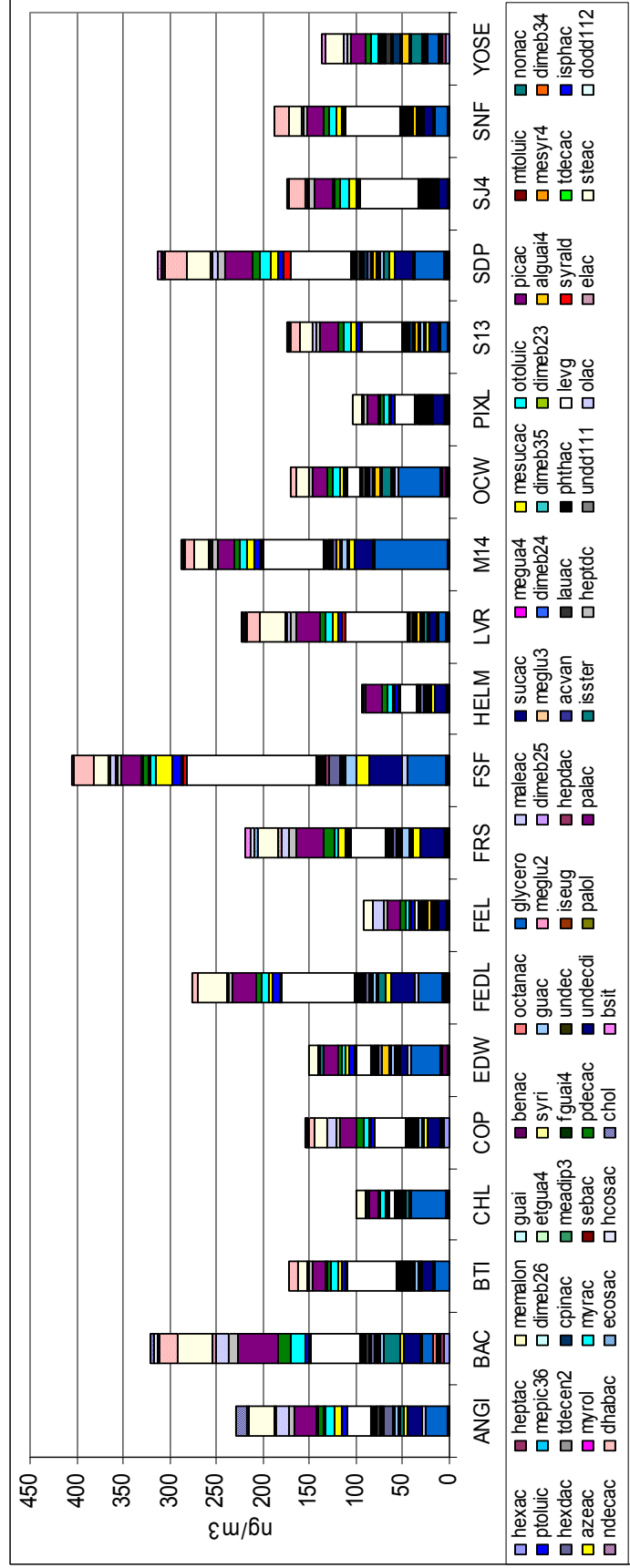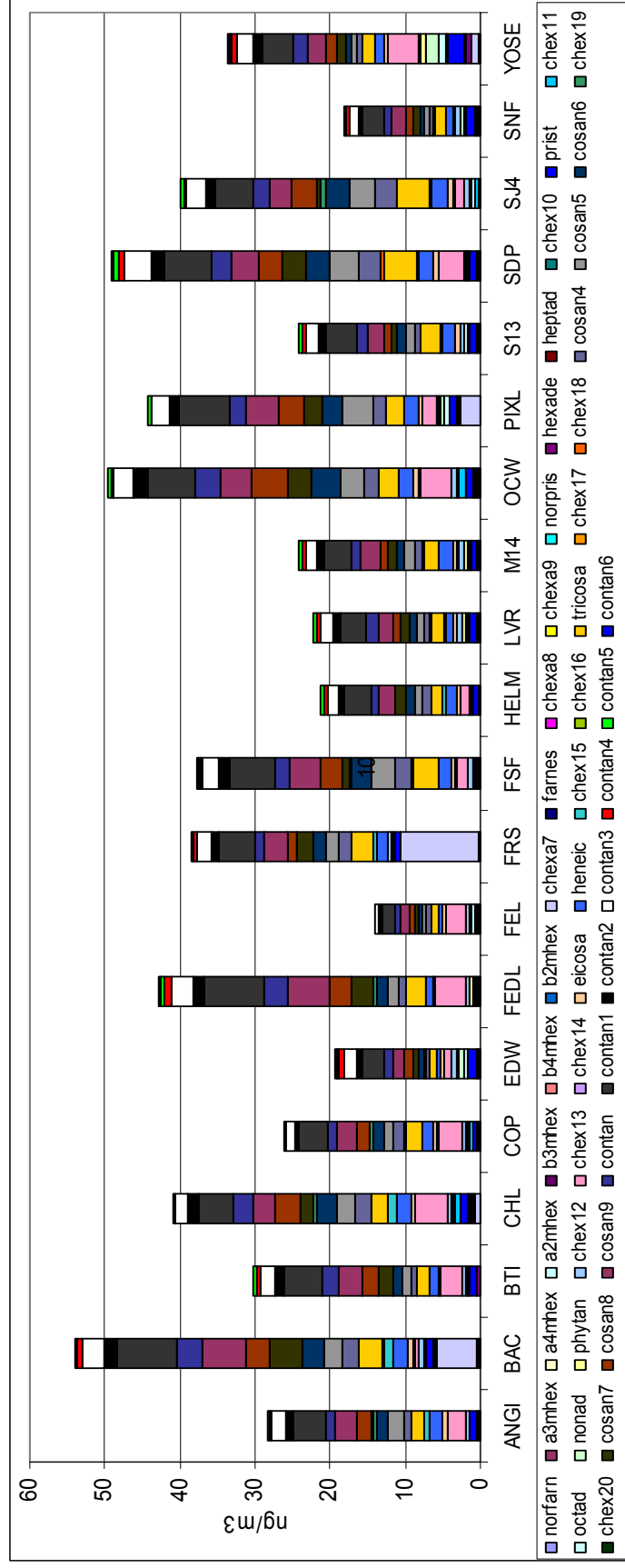
5-12

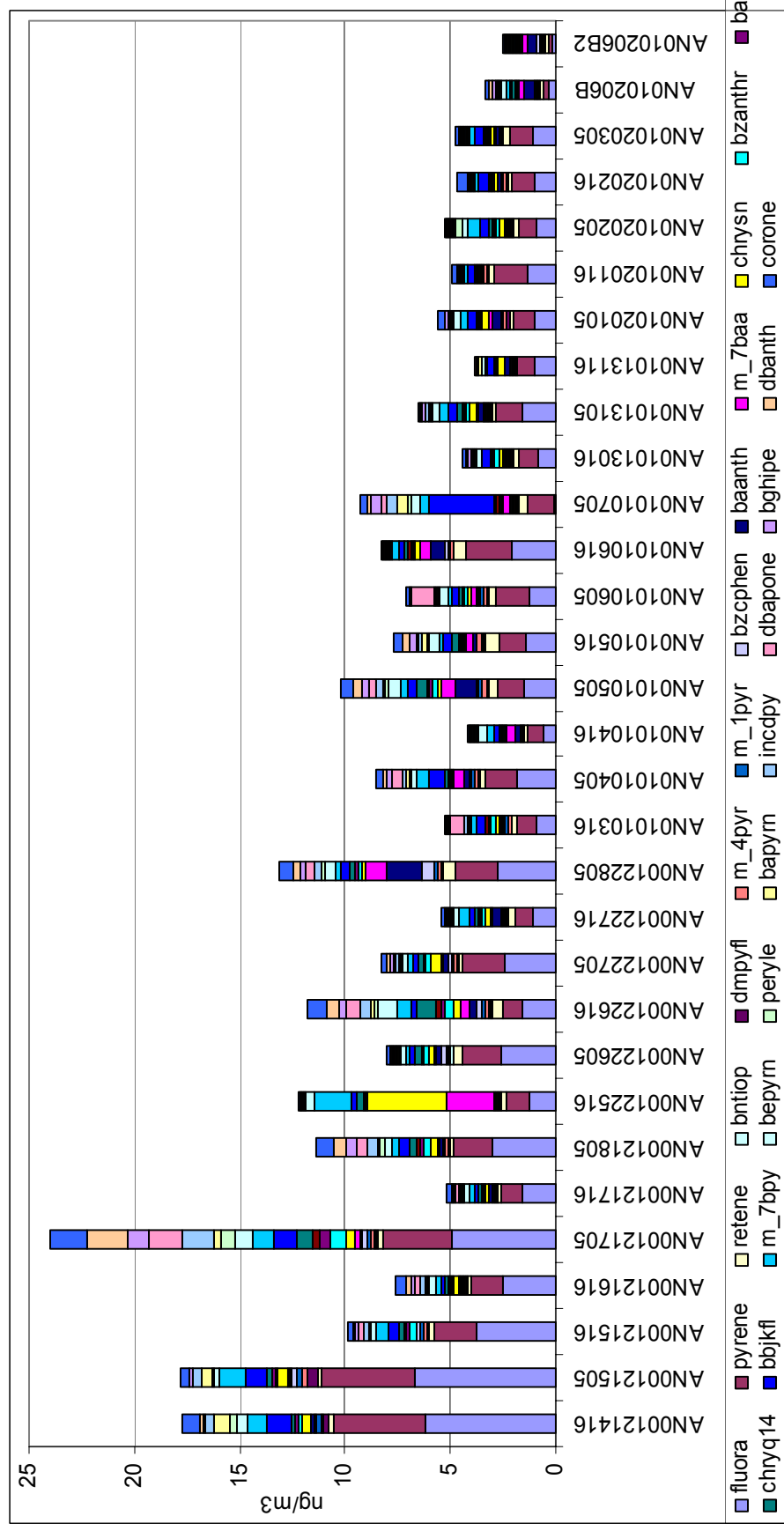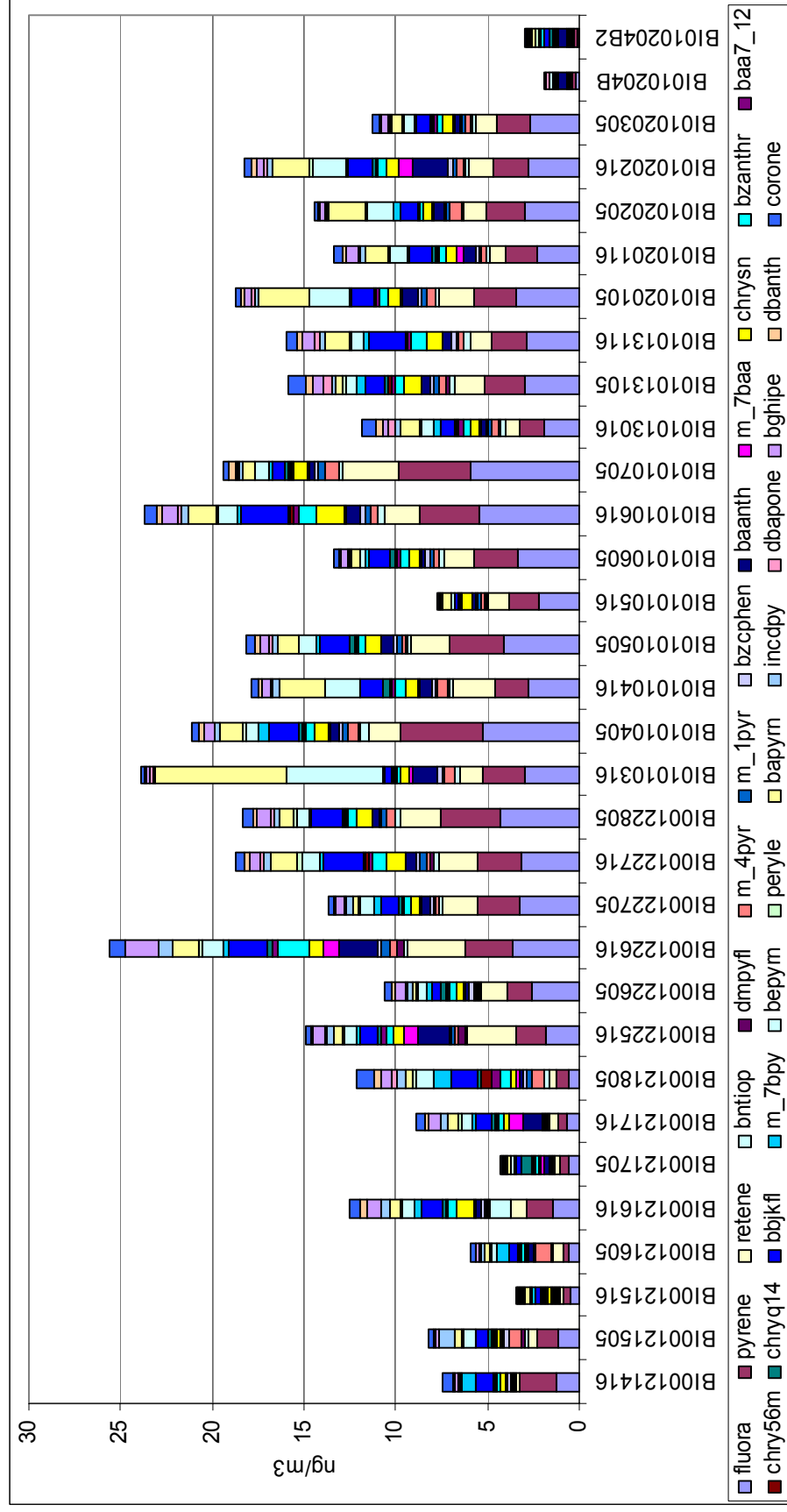**Figure 5-4.** Polar Organic Annual Average concentrations for the 20 Satellite sites.

Figure 5-5. High MW Alkane Annual Average concentrations for the 20 Satellite sites.

5-16

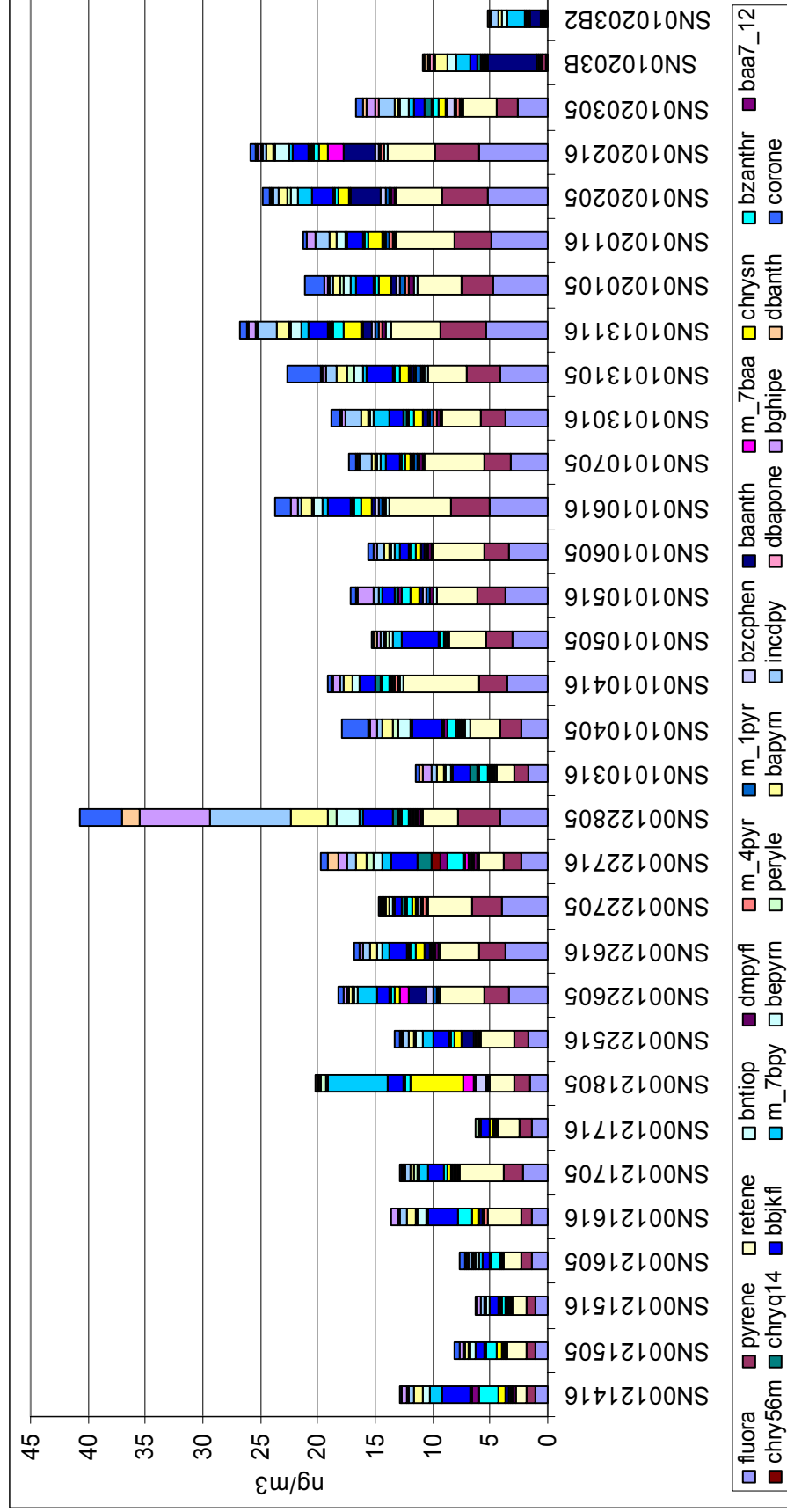**Figure 5-6.** High MW PAH concentrations for the Angiola site.

Figure 5-7. High MW PAH concentrations for the Bethel Island site.

5-20

Figure 5-8. High MW PAH concentrations for the Sierra Nevada Foothills site
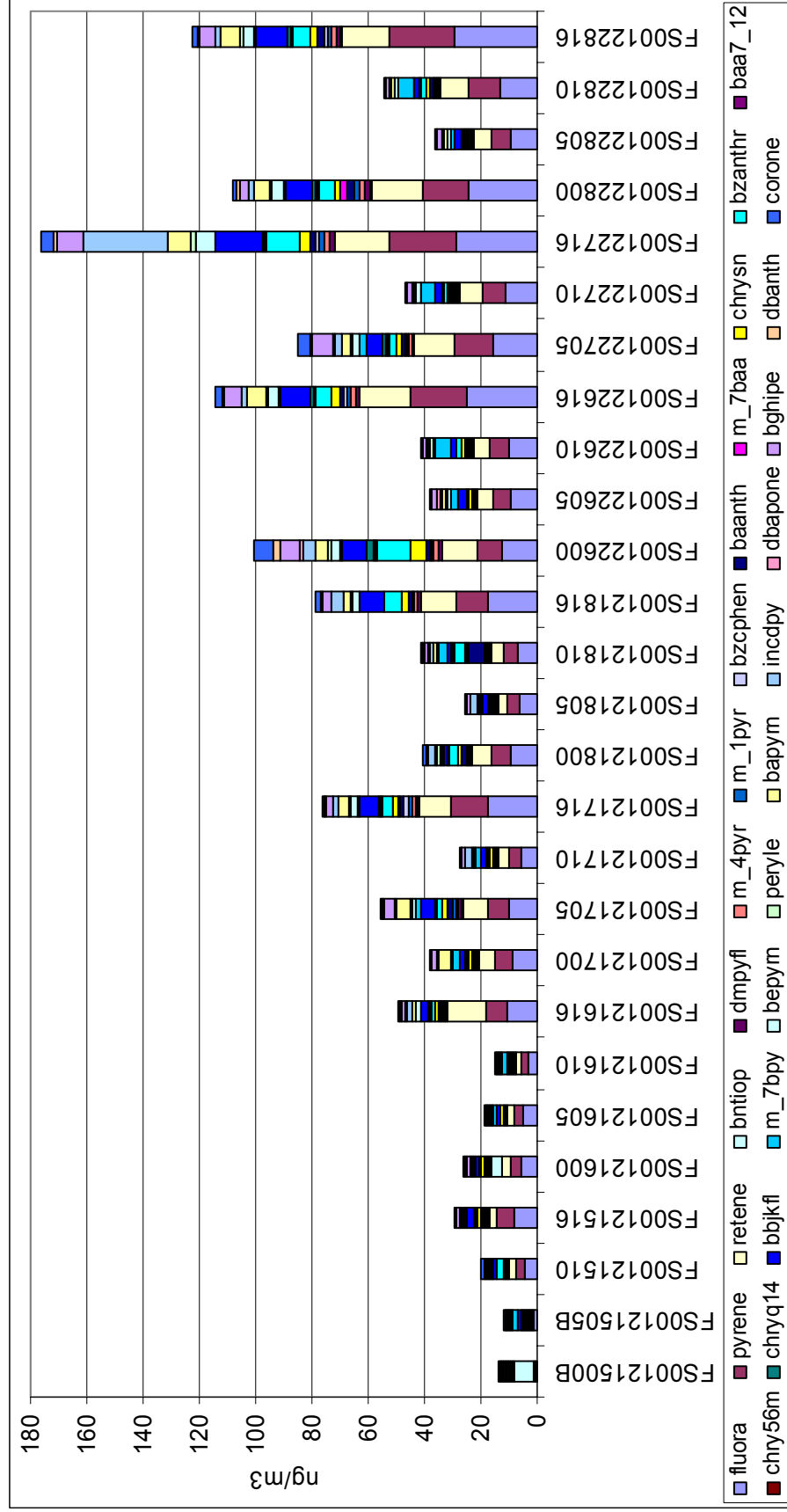
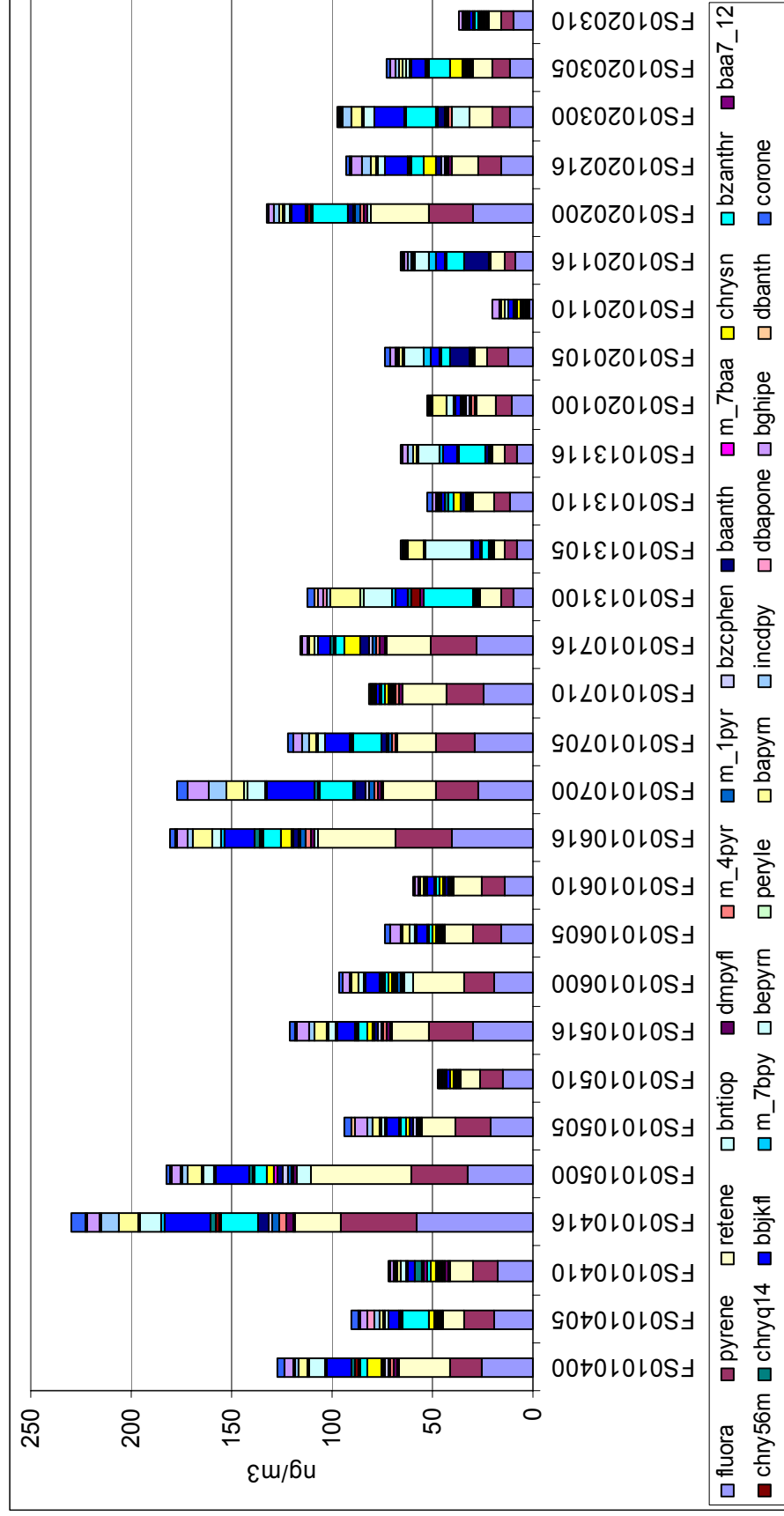**Figure 5-9.** High MW PAH concentrations for the Fresno Site Part One.

Figure 5-10 High MW PAH concentrations for the Fresno site Part Two.

5-26